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Electrochemical approaches to the determination of rate constants for the activation step in atom transfer radical polymerization

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ABSTRACT

Direct determination of ATRP activation rate constant, k_{act}, is typically limited to slow or moderately fast reactions: $k_{act} < 10^2\ mol^{-1}\ dm^3\ s^{-1}$ were determined by classical techniques, such as chromatography, spectrophotometry, NMR, *etc*. Therefore, these techniques are inadequate to study the fastest, and most useful, ATRP systems, such as the most frequently used Cu complexes with tris[2-(dimethylamino)ethyl] amine (Me_6TREN), tris(2-pyridylmethyl)amine (TPMA) and substituted TPMA. In this study, electrochemical methods have been used to investigate the kinetics of activation of a series of typical ATRP initiators (RX) by $[Cu^IL]^+$ (L = Me_6TREN, TPMA or *N,N,N′,N″,N″*-pentamethyldiethylenetriamine, PMDETA) in MeCN. Both high ($>10^4\ mol^{-1}\ dm^3\ s^{-1}$) and low k_{act} values have been measured. Analysis of the collected data showed that k_{act} depends on E° of the catalyst, molecular structure of RX, and nature of the halogen atom. Although usually values of k_{act} increase with decreasing standard reduction potential of $[Cu^{II}L]^{2+}$, there is no well-defined correlation between the two parameters. Instead, k_{act} gives good and useful linear correlations with the standard reduction potential of $[XCu^{II}L]^+$, and with K_{ATRP} or Gibbs free energy of C-X bond dissociation.

1. Introduction

Atom transfer radical polymerization (ATRP) is a very important controlled radical polymerization process. It enables polymerization of a vast range of monomers for the preparation of polymeric materials with well-defined architecture, pre-determined chain length and low dispersity [1–3]. The general mechanism of atom transfer radical polymerization (ATRP) involves an equilibrium between dormant species containing a carbon-halogen bond (RX) and active, propagating radical species ($R^\bullet$) (Scheme 1). The reaction is catalyzed by transition metal complexes, mainly Cu with polydentate amine ligands [4–6]. The ATRP equilibrium is generally well-shifted toward the reagents RX and Cu^I ($K_{ATRP} << 1$), giving a low radical concentration in the reaction mixture and so minimizing the frequency of termination reactions between radicals [7,8]. Chains spend most of their time in the dormant state and the average life of “living” polymers is greatly extended. The resulting controlled polymerization is characterized by linearity of $\log([M]_0/[M])$ vs. t plots (M = monomer) up to high conversions, pre-determined molecular weights, preservation of most chain-end functionalities and low dispersity ($M_w/M_n < 1.3$ for a well-controlled reaction; M_w and M_n are weight average and number average molecular weights, respectively).

Although K_{ATRP} should be small to ensure low radical concentration, both activation (k_{act}) and deactivation (k_{deact}) rate constants should be high to ensure fast exchange between dormant and active species. Typically, once a radical is generated it adds only to a few monomer units before being quickly deactivated by the Cu^{II} complex. The quick activation/deactivation cycle results in simultaneous and homogenous growth of all polymer chains.

While both k_{act} and k_{deact} are important, it has been shown that k_{act} is much more sensitive than k_{deact} to the molecular structures of both catalyst and initiator (RX) [7,8]. Consequently, k_{act} is one of the main indicators of the activity of the catalyst/initiator couple and could be used alone to obtain a rough estimate of the order of magnitude of K_{ATRP}. The equilibrium constant can be used to relate the rate of polymerization, R_p, to the concentration of the

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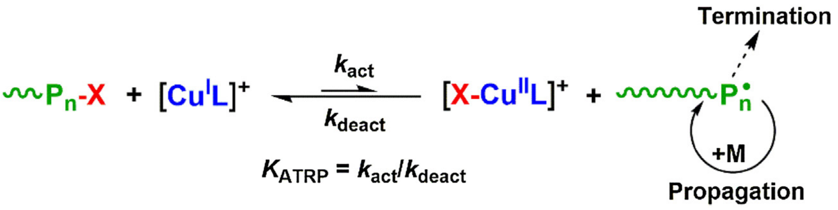


Scheme 1. General ATRP mechanism.

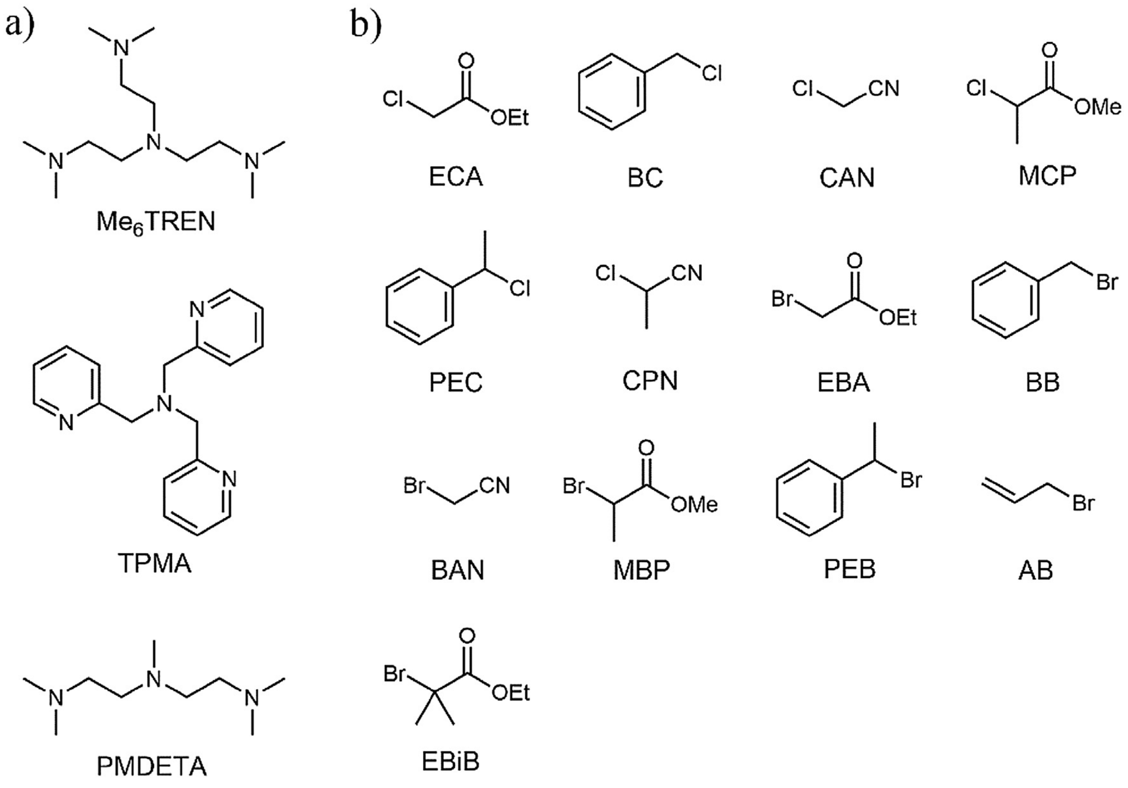
propagating radicals:

$$R_p = k_p C_M C_{R^\bullet} = k_p K_{ATRP} C_M C_{RX} \frac{C_{Cu^I}}{C_{Cu^{II}}} = k_p \frac{k_{act}}{k_{deact}} C_M C_{RX} \frac{C_{Cu^I}}{C_{Cu^{II}}} \quad (1)$$

where k_p is the propagation rate constant, and C_M and C_{RX} are monomer and initiator concentrations. Therefore, information on k_{act} values is important for choosing the optimal experimental conditions [9], e.g. for selecting the best catalyst/initiator couple in a specific polymerization system. Indeed, since some initiators mimic the dormant chain ends (e.g. $PhCH_2X$ for polystyrene, $CH_3CH(X)CO_2CH_3$ for poly(methyl acrylate), $CH_3CH(X)CN$ for polyacrylonitrile, etc.), these data are relevant for the characterization of the activation step during polymerization. In this context, the effect of the chain length is considered to be rather weak as previously shown by Fukuda and Goto [10], although the so-called penultimate effect was observed for a few monomers such as methacrylates [11,12].

Recently, several efficient methods have been developed for the generation and regeneration of the active Cu^I catalyst. Knowledge of k_{act} allows the choice of the best methodology for any polymerization system. Catalysts with low activity are suitable for the normal ATRP method, where Cu^I at a high concentration is directly injected in the reaction mixture. More active catalysts can be employed at very low concentrations (ppm levels), provided that the active Cu^I species is continuously regenerated [13] as in ARGET ATRP [14,15], SARA ATRP [16], electrochemically mediated ATRP (*e*ATRP) [17–24] and photoinduced ATRP [25–27].

The activation rate constants of various ATRP systems have been already reported in the literature. However, only in a few cases relatively fast reactions were analyzed by stopped-flow [28,29] or electrochemical techniques [30–34]. In most cases, the employed methodologies (gas or liquid chromatography [35–43], spectrophotometry [44–47], NMR [10,48]) were suitable only for the characterization of very slow reactions. Therefore, most of the published data for the most active and successful catalysts (namely, Cu complexes with PMDETA, TPMA and Me_6TREN ligands) were estimated on the basis of the assumption that the k_{act} ratio of two different alkyl halides (e.g. $k_{act,(RX)_1}/k_{act,(RX)_2}$) remains unaffected by changing the nature of the Cu^I complex, which is questionable considering the inner sphere nature of the



Scheme 2. Structures of the investigated copper ligands (a) and ATRP initiators (b).