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Electrochemical Atom Transfer Radical Polymerization in Miniemulsion with a Dual Catalytic System

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Abstract

An electrochemical approach was used to control atom transfer radical polymerization (ATRP) of *n*-butyl acrylate (BA) in miniemulsion. Electropolymerization required a dual catalytic system, composed of an aqueous phase catalyst and an organic phase catalyst. This allowed shuttling the electrochemical stimulus from the working electrode (WE) to the continuous aqueous phase and to the dispersed monomer droplets. As aqueous phase catalysts, the hydrophilic Cu complexes with the ligands *N,N*-bis(2-pyridylmethyl)-2-hydroxyethylamine (BPMEA), 2,2'-bipyridine (bpy), and tris(2-pyridylmethyl)amine (TPMA) were tested. As organic phase catalysts, the hydrophobic complexes with the ligands bis(2-pyridylmethyl)-octadecylamine (BPMODA) and bis[2-(4-methoxy-3,5-dimethyl-pyridylmethyl)octadecylamine (BPMODA*) were evaluated. Highest rates and best control of BA electropolymerization were obtained with the water-soluble Cu/BPMEA used in combination with the oil-soluble Cu/BPMODA*. The polymerization rate could be further enhanced by changing the potential applied at the WE. Differently from traditional ATRP systems, reactivity of the dual catalytic system did not depend on the redox potential of the catalysts but instead depended on the hydrophobicity and partition coefficient of the aqueous phase catalyst.

Graphical Abstract

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Notes

The authors declare no competing financial interest.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.6b02037. Experimental section, polymerization procedures, characterization of aqueous phase catalysts, and additional polymerization results (PDF)

1. INTRODUCTION

Dispersed media, such as miniemulsions, are useful eco-friendly systems, less toxic, and less expensive than most organic solvents. In particular, oil-in-water miniemulsions have many applications, enabled by the submicrometer size of the dispersed oil droplets, by the large array of possible hydrophobic reactants, and by the excellent mass and heat transport properties.^{1–5}

Combining eco-friendly (mini)emulsions with electrosynthetic methods offers an additional advantage, since the use of electrons as reagents does not involve the formation of side products observed when using reducing or oxidizing agents.⁶ As a result, dispersed media has been used for both direct and mediated electrosyntheses, including reduction of organic halides,^{7,8} reductive dimerization,⁹ removal of pollutants,¹⁰ and formation of carbon–carbon bonds.¹¹ For example, the Monsanto process produces annually 1 billion kg of adiponitrile (a precursor of nylon-66) by electrosynthesis in emulsion.¹²

Despite the utility of organic electrosynthesis in dispersed media, the electrochemical approach has not yet been applied to controlled radical polymerizations, a class of reactions successfully performed in dispersed media. In particular, atom transfer radical polymerization (ATRP) has been carried out by traditional (nonelectrochemical) methods in emulsions,^{13–17} microemulsions,^{18,19} miniemulsions,^{20–22} and inverse miniemulsion²³ with the production of well-defined latexes. Therefore, our goal was to extend the use of electrosynthesis to the field of polymerization in dispersed media, realizing the electrochemically mediated ATRP of *n*-butyl acrylate (BA) in miniemulsion.

ATRP is a controlled radical polymerization process, commonly used to create polymers with predetermined molecular weight (MW) and narrow molecular-weight distribution ().^{24–31} Moreover, ATRP can control copolymer composition (e.g., block and gradient copolymers), topology (e.g., stars and bottlebrushes), and location of functional groups (e.g., α -, ω -, or both, periphery or core functional stars, and side-group functional brushes).^{32–37} A wide range of monomers is available for ATRP, including (meth)acrylates, styrenes, acrylamides, acrylonitrile, and methacrylic acid.^{38–42}

Scheme 1 shows the mechanism of ATRP mediated by a copper–amine ligand catalyst (Cu/L). Cu^I/L activates an alkyl halide initiator (R–X) to form a radical (R•) and a deactivator complex (X–Cu^{II}/L). R• (or the polymeric radical, P_n•) propagates by adding of a few monomer units, before being quickly deactivated by the X–Cu^{II}/L complex to re-form the dormant polymeric species (P_n–X) and the original activator complex (Cu^I/L). In miniemulsion ATRP, hydrophobic catalyst, initiator, and monomer are typically confined in the organic phase droplets.

The originally developed ATRP procedure required more than 10 000 ppm of Cu catalysts (compared to monomer molar concentration); therefore, extensive purification of the products was necessary.^{43–49} Currently, however, several catalyst (re)-generation methods allow performing ATRP reactions with low ppm levels of catalysts; these techniques include activators regenerated by electron transfer (ARGET) ATRP,^{50–58} initiators for continuous activator regeneration (ICAR) ATRP,^{50,59–65} supplemental activator and reducing agent (SARA) ATRP,^{66–73} photoinduced ATRP (photoATRP),^{74–85} and electrochemically mediated ATRP (eATRP, the method used in this work).^{86–97}

In eATRP, reduction of X–Cu^{II}/L to Cu^I/L occurs by means of a cathodic current flowing from a metal working electrode (WE, Scheme 1).^{98,99} Rate and control of the polymerization are modulated by the electrochemical parameters applied to the system, such as current intensity, applied potential (E_{app}), or total injected electric charge.⁸⁸ “On–off” polymerization can be obtained by simply stepping E_{app} between negative and positive values (i.e., by reduction and reoxidation of the catalyst),⁴¹ whereas the rate of polymerization (R_p , eq 1)³⁰ can be enhanced until mass-transfer limit by quantitatively reducing the catalyst to Cu^I/L.¹⁰⁰

$$R_p = k_p K_{ATRP} \frac{[R-X][Cu^I/L]}{[X-Cu^{II}/L]} [M] \quad (I)$$

where k_p is the monomer propagation rate constant and K_{ATRP} is the ATRP equilibrium constant.

An advantage of eATRP is that it relies on the application of an external stimulus, similarly to photomediated ATRP. Although several heterogeneous photopolymerizations have been achieved,^{101,102} this technique is limited by the opacity of most heterogeneous solution and by the formation of photodegradation products. Moreover, photopolymerization usually required high UV light intensity,¹⁰³ dedicated setups,^{103,104} and/or provided limited conversion (< 50%).^{101,102}

Electropolymerization under heterogeneous conditions is also challenging because in (mini)emulsion electrode and reactants are separated: the electrode is in contact with the continuous aqueous phase, while polymerization reactants (monomer, initiator, and radicals) are dispersed in the organic phase. Therefore, to trigger polymerization the electrochemical stimulus must first reach the aqueous phase (crossing the first electrode|liquid interface) and then shuttle to the dispersed phase (crossing the second liquid|liquid interface). Moreover,

mini-emulsion *e*ATRP poses an additional challenge in comparison to most organic reactions because radicals must be continuously activated/deactivated after the electrochemical stimulus has reached the organic phase.

To establish efficient electrochemical communication in mini-emulsion *e*ATRP, we used a dual catalytic system composed of two distinct copper catalysts (one hydrophilic and one hydrophobic). The two mediators created an unbroken connection from the electrode surface to P_n-X in the monomer droplets, which enabled controlled polymerization and resulted in the production of well-defined poly(*n*-butyl acrylate) (PBA) latexes.

To summarize, our goals were the following: (i) extend the use of electrosynthesis to the field of heterogeneous polymerizations by realizing *e*ATRP of BA in mini-emulsion (with a dual catalytic system) and (ii) understand how the dual catalytic system communicated at the electrode|liquid and liquid|liquid interfaces. The proper balance between redox potentials and hydrophilic/hydrophobic properties of the dual catalytic system provided efficient electrocatalysis and yielded well-defined polymers by *e*ATRP in mini-emulsion.

2. RESULTS AND DISCUSSION

Selection of the Appropriate Dual Catalyst Combinations

Assembling a dual catalytic system required selection of two different catalysts, each suitable for the aqueous or for the organic phase. For the continuous aqueous phase, we examined common water-soluble ATRP catalysts such as Cu/TPMA and Cu/bpy (a mole ratio Cu/bpy = 1:2 was used). Moreover, a strongly hydrophilic ligand with a pendant OH group, *N,N*-bis(2-pyridylmethyl)-2-hydroxyethylamine (BPMEA), was designed to match the reactivity of hydrophobic BPMODA (structure in Figure 1, synthesis in the Supporting Information).

In the dispersed organic phase, hydrophobic copper ligands have been used, such as bis(2-pyridylmethyl)octadecylamine (BPMODA).¹⁰⁵ The octadecyl chain of BPMODA provided sufficient hydrophobicity to confine the copper complex to the organic phase. However, the ATRP activity of Cu^I/BPMODA was low, so that relatively high catalyst loadings were required to maintain a suitable R_p .¹⁰⁶ Polydentate ligands such as tris[2-(dimethylamino)ethyl]amine (Me₆TREN) or tris(2-pyridylmethyl) amine (TPMA) can enhance catalytic activity^{107,108} by 10³–10⁵ times with respect to the conventionally used Cu/bpy.^{1,3–5,24,109,110} Copper complexes with Me₆TREN and TPMA, however, are not hydrophobic enough to be confined in the organic phase; therefore, specifically designed active oil-soluble ligands were required. Mini-emulsion ARGET ATRP using a more active ligand, BPMODA modified with six electron donor groups, bis[2-(4-methoxy-3,5-dimethyl)pyridylmethyl] octadecylamine (BPMODA*), was previously reported.¹⁰⁶ Heterogeneous polymerization showed linear evolution of MW with conversion and narrow molecular-weight distribution (MWD) using only 250 ppm of Cu complex. Herein, both Cu/BPMODA and Cu/BPMODA* were tested as organic phase catalysts for mini-emulsion *e*ATRP.

Distribution of Catalysts between Aqueous and Organic Phases

Designing an efficient dual catalytic system in miniemulsion required investigating how the catalysts were distributed between the aqueous phase and the BA droplets, which depended on the hydrophobicity of the copper complexes. Catalyst distribution was determined by UV-vis spectrometry. First, a calibration curve was obtained by preparing CuBr_2/L solutions at different concentrations (0.1–20 mM in water, see Figure S1 in the Supporting Information). Then, the calibration curve was used to calculate the fraction of catalyst present in the aqueous phase in a water/BA mixture at equilibrium ($[\text{CuBr}_2/\text{L}]_{\text{aq}}/[\text{CuBr}_2/\text{L}]_{\text{tot}}$, Table 1 and Figure S2). Compared to $\text{Cu}^{\text{II}}/\text{L}$, the less hydrophilic Cu^{I} (reduced) complexes have a lower net positive charge ($\text{Cu}^{\text{I}}/\text{L}$ is neutral when coordinated by Br^- , as $\text{Br}-\text{Cu}^{\text{I}}/\text{L}$). Therefore, $\text{Cu}^{\text{I}}/\text{L}_{\text{aq}}$ has a higher tendency to migrate to the organic phase. Unfortunately, the limited stability of Cu^{I} complexes in water¹¹¹ prevented accurate determination of their partition coefficient.

The partition experiments indicated that $\text{CuBr}_2/\text{BPMEA}$, CuBr_2/bpy , and $\text{CuBr}_2/\text{TPMA}$ strongly preferred the aqueous phase (>88% at 60 °C) and therefore were selected as aqueous phase catalysts ($\text{Cu}^{\text{II}}/\text{L}_{\text{aq}}$). The hydrophilicity increased in the order $\text{CuBr}_2/\text{BPMEA}_{\text{aq}} < \text{CuBr}_2/\text{bpy}_{\text{aq}} < \text{CuBr}_2/\text{TPMA}_{\text{aq}}$, the latter being very hydrophilic as it was completely located in the aqueous phase (Figure 2A). Conversely, according to previous reports,¹⁰⁶ $\text{CuBr}_2/\text{BPMODA}$ and $\text{CuBr}_2/\text{BPMODA}^*$ had a high preference for the organic phase ($[\text{CuBr}_2/\text{L}]_{\text{water}}/[\text{CuBr}_2/\text{L}]_{\text{tot}} = 0.30$ and 0.10 for $\text{L} = \text{BPMODA}$ and BPMODA^* , respectively, with $[\text{CuBr}_2/\text{L}]_{\text{tot}} = 2.5$ mM and $T = \text{room temperature, RT}$). Therefore, $\text{CuBr}_2/\text{BPMODA}$ and $\text{CuBr}_2/\text{BPMODA}^*$ were used as organic phase catalysts ($\text{Cu}^{\text{II}}/\text{L}_{\text{org}}$), as a hydrophobic Cu^{II} complex was required to have a sufficient amount of deactivator in the monomer droplets.

Electrochemical Properties of the Catalysts

Information on the redox properties of the catalysts was used to choose the appropriate dual catalyst combinations and to select E_{app} during electropolymerization. The complexes were investigated by cyclic voltammetry (CV) in various solvents that mimicked polymerization conditions: aqueous phase (water + 0.1 M NaBr), organic phase (BA + 0.1 M *n*-Bu₄NPF₆), and miniemulsion (the composition of the heterogeneous solvent is listed in Table 3). The CV response was different for hydrophilic and hydrophobic complexes and depended on the solvent.

In each phase/solvent, the hydrophilic catalysts $\text{Cu}^{\text{II}}/\text{L}_{\text{aq}}$ presented a quasi-reversible ET (with peak separation between 120 and 60 mV) which indicated the presence of well-defined and stable copper complexes (Figure 3, Figures S3 and S4). The CVs also allowed measuring the half-wave potentials of the complexes as $E_{1/2} = (E_{\text{pc}} + E_{\text{pa}})/2$, where E_{pc} and E_{pa} are the anodic and cathodic peaks potentials, respectively (Table 2).

Conversely, the hydrophobic catalysts $\text{Cu}^{\text{II}}/\text{L}_{\text{org}}$ showed a quasi-reversible electrochemical response only when examined in organic phase (BA/anisole 1/1, Figure S5), whereas a tiny reduction current ($i < 1 \mu\text{A}$) was detected in both aqueous phase and miniemulsion (Figure S6). In aqueous phase, the complex was poorly soluble. In miniemulsion, the low current

indicated that the electrode was disconnected from $\text{Cu}^{\text{II}}\text{L}/_{\text{org}}$: the catalyst was well-confined in the monomer droplets, while the electrode was in contact with the aqueous continuous phase.

Half-wave potentials were used to assess the electrochemical reactivity of the complexes (Figure 2 and Table 2). Among the aqueous phase catalysts, the strongest reducing agent (i.e., most active complex) was $\text{Cu}^{\text{I}}/\text{TPMA}$, followed by $\text{Cu}^{\text{I}}/\text{BPMEA}$ and $\text{Cu}^{\text{I}}/\text{bpy}$ (the same trend was maintained in each phase). Among the organic phase catalysts, $\text{Cu}^{\text{I}}/\text{BPMODA}^*$ was a better reducing agent than $\text{Cu}^{\text{I}}/\text{BPMODA}$.

The reactivity of the catalysts was also assessed by CV under polymerization conditions, i.e., in miniemulsion in the presence of the initiator ethyl α -bromoisobutyrate, EBiB (Figure 3B). Under such conditions, the CV was made irreversible (or less reversible) by the occurrence of the electrochemical catalytic cycle in Scheme 1: the electrogenerated Cu^{I} complex was oxidized by occurrence of the ATRP reaction, and the produced $\text{Cu}^{\text{II}}/\text{L}$ was further catalytically reduced at the electrode surface. This electrochemical cycle increased the cathodic current proportionally to the activity of the catalyst,^{70,111} which followed the same order provided by analysis of the redox potentials (Figure 2).

Half-wave potentials of the Cu complexes changed with solvent, with $E_{1/2}$ in water < $E_{1/2}$ in miniemulsion < $E_{1/2}$ in organic phase (Table 2). The $E_{1/2}$ shift between water and organic solvent is well documented in the literature, as ATRP catalysts are stronger reducing agents in water than they are in organic solvent.^{111,112} Instead, the $E_{1/2}$ shift between water and miniemulsion was mostly due to the partial solubility of BA in water,¹¹³ which affected the redox properties of $\text{Cu}^{\text{I}}/\text{L}_{\text{aq}}$ in miniemulsion by reducing solvent polarity (Figure S7).¹¹⁴

Overall, the electrochemical response in miniemulsion was similar to that of a typical homogeneous solvent. Absorption of surfactant molecules played little or no role in modifying the electrode|liquid interface,¹¹⁵ indicating that electrochemical methods could be successfully applied to this dispersed system. The CVs recorded in miniemulsion under polymerization conditions (Figure 3B) were used to select the potential applied during eATRP. $E_{\text{app}} = E_{\text{pc}}$ was selected, which allowed a quite fast reduction of Cu^{II} to Cu^{I} in the aqueous phase.

eATRP in Miniemulsion

A series of experiments were conducted to elucidate the role of the catalyst in each phase during miniemulsion eATRP. The composition of both aqueous phase and organic phase is listed in Table 3. The miniemulsion was prepared by ultrasonic treatment at 0 °C to prevent undesirable reactions (more details in the Supporting Information). Preparation of the dual catalyst mixture was simple, as it just required adding a small quantity of a second ligand. Sodium dodecyl sulfonate (SDS) was used as surfactant, which required addition of 0.1 M NaBr to prevent competitive complexation between SDS and the $\text{Br}-\text{Cu}^{\text{II}}\text{L}^+$ deactivator.¹¹⁶ NaBr also increased solution conductivity, without destabilizing the dispersed particles (Figure S8). Miniemulsions generally have very good solvent properties, so that they can easily strip an absorbed layer of polymer from an electrode;⁶ this is a clear advantage as it avoids passivation of the electrode surface during eATRP.

As expected, no polymerization was observed without applied current (in the presence of both CuBr₂/BPMEA and CuBr₂/BPMODA*, Table 4, entry 1), confirming that the active Cu^I catalyst must be produced at the WE to trigger the polymerization.

Upon application of a negative $E_{app} = -0.3$ V vs SCE, a cathodic current was recorded (see Figure S9 as example) and polymerization was started by reduction of Cu^{II} to Cu^I. However, miniemulsion polymerization was slow in the presence of only Cu^{II}/L_{org} (<7% conversion in 24 h when using Cu^{II}/BPMODA_{org} or Cu^{II}/BPMODA*_{org} as in Table 4, entries 2 and 3). Reduction of Cu^{II}/L_{org} in miniemulsion was ineffective, and thus the current flow was small (0.3 C of total consumed charge, Q). For comparison, reduction of CuBr₂/BPMODA* in traditional homogeneous solvent (DMF) was fast and led to well-controlled eATRP (Figure S10). Overall, miniemulsion eATRP could not be controlled using Cu^{II}/L_{org} as the only catalyst, confirming that the electrode was disconnected from the monomer droplets.

Conversely, electropolymerization was fast in the presence of only Cu^{II}/L_{aq}, reaching 54% and 66% conversion with CuBr₂/bpy_{aq} and CuBr₂/BPMEA_{aq}, respectively (Table 4, entries 4 and 5). However, polymerization was completely uncontrolled, with dispersity > 4 and MW not increasing linearly with conversion. These results suggested that not enough Cu^{II} deactivator was present in organic phase when using hydrophilic catalysts, undermining polymerization control.

eATRP with a dual catalyst, Cu^{II}/L_{aq} + Cu^{II}/L_{org}, provided PBA with much better control (Table 4, entries 6–11); linear logarithmic kinetic plots and linear increase of MW with conversion were observed (Figure 4). This indicated that a dual catalytic system was required to establish effective communication from the electrode to the aqueous and organic phases. Several catalyst combinations were investigated to answer the following questions: (i) What are the required characteristics of the catalyst combination to obtain fast and well-controlled miniemulsion eATRP? (ii) How is the electrochemical stimulus transported between aqueous phase and organic phase? In order to better compare the polymerization results, $E_{app} = E_{pc}$ was applied for each catalyst combination (Figure 3B), so that the rate of Cu^I electrogeneration was similar in each case.

Performance of dual catalysts was evaluated in terms of polymer dispersity and apparent rate of polymerization (k_p^{app}). With CuBr₂/BPMODA_{org}, the highest k_p^{app} was observed in the presence of CuBr₂/BPMEA_{aq}, followed by CuBr₂/bpy_{aq} and by CuBr₂/TPMA_{aq}. However, polymerizations were poorly controlled, with > 1.5 and MW not matching well the theoretical values (Figures S11 and S12).

Better control was obtained with CuBr₂/BPMODA*_{org}, a more active catalyst that was more suitable for a low ppm ATRP process. In this case, low $\bar{M}_w/\bar{M}_n$ was observed with each tested Cu^{II}/L_{aq}. However, the best catalyst combination was CuBr₂/BPMEA_{aq} + CuBr₂/BPMODA*_{org}, which provided the lowest $\bar{M}_w/\bar{M}_n = 1.19$ and the fastest polymerization rate. Interestingly, the two catalysts in the dual system are both tridentate and structurally similar (Figure 1). DLS analysis showed that miniemulsion particles were stable during the eATRP (Figure S8): particle size was very similar before and after the polymerization (91 and 101 nm, respectively, for the polymerization conditions in Table 4, entry 10).

Unexpectedly, with either $\text{CuBr}_2/\text{BPMODA}_{\text{org}}$ or $\text{CuBr}_2/\text{BPMODA}^*_{\text{org}}$, the apparent polymerization rate (k_p^{app}) followed an unusual order: $\text{CuBr}_2/\text{BPMEA}_{\text{aq}} > \text{CuBr}_2/\text{bpy}_{\text{aq}} > \text{CuBr}_2/\text{TPMA}_{\text{aq}}$. This reactivity trend disagrees with typical ATRP systems,^{20c,27} as k_p^{app} was not determined by the redox properties of the complex^{88,111} (k_p^{app} did not increase with decreasing half-wave potentials, Figure 2B). However, it has already been shown that dispersed media can trigger different reaction pathways.⁹ Indeed, the k_p^{app} trend observed in miniemulsion eATRP was determined by the hydrophobicity of $\text{Cu}/\text{L}_{\text{aq}}$, which suggested a mechanism for the communication between $\text{Cu}^{\text{I}}/\text{L}_{\text{aq}}$ and $\text{Cu}^{\text{II}}/\text{L}_{\text{org}}$ based on catalysts' partition between oil and water phases.

Proposed Mechanism of eATRP in Miniemulsion

Scheme 2 presents the proposed mechanism of miniemulsion eATRP. First, the catalyst in the continuous aqueous phase was reduced to the active $\text{Cu}^{\text{I}}/\text{L}_{\text{aq}}$ complex at the WE:

Then, electrochemical communication occurred between water and organic phase, which contained monomer and initiator. This can happen in two ways: (i) ET between $\text{Cu}^{\text{I}}/\text{L}_{\text{aq}}$ and $\text{Cu}^{\text{II}}/\text{L}_{\text{org}}$ at the water|oil interface or (ii) migration of $\text{Cu}^{\text{I}}/\text{L}_{\text{aq}}$ to the organic phase. The first pathway is unlikely because the rate of polymerization did not follow the electrochemical reactivity of the catalyst (Figure 2B), indicating that interfacial ET was not the rate-determining step. Instead, reactivity of the catalysts strongly supported the second pathway (migration of $\text{Cu}^{\text{I}}/\text{L}_{\text{aq}}$) because k_p^{app} was determined by the partition of the aqueous phase catalyst (Figure 2A). $\text{Cu}/\text{BPMEA}_{\text{aq}}$ and $\text{Cu}/\text{bpy}_{\text{aq}}$ were the most active catalysts because they were sufficiently distributed in the organic phase (ca. 10%, Table 1). Therefore, kinetics of miniemulsion eATRP suggested the model of a dynamic heterogeneous system, in which $\text{Cu}^{\text{I}}/\text{L}_{\text{aq}}$ was not compartmentalized in the aqueous phase but could cross the water|oil interface.

Once $\text{Cu}^{\text{I}}/\text{L}_{\text{aq}}$ migrated to the monomer droplets (which determined k_p^{app}), it could be involved in two different reaction pathways. The first was reduction of $\text{Cu}^{\text{II}}/\text{L}_{\text{org}}$, followed by chain end activation by $\text{Cu}^{\text{I}}/\text{L}_{\text{org}}$ (pathway A in Scheme 2):

The second was direct activation of the chain end (pathway B in Scheme 2):

The relative importance of pathways A and B depended on the redox potential difference between hydrophilic and hydrophobic catalysts inside the monomer droplets ($E_{1/2}$ in Table 4). If $\Delta E_{1/2} < 0$ ($E^\circ_{\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}_{\text{aq}}} < E^\circ_{\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}_{\text{org}}}$), $\text{Cu}^{\text{I}}/\text{L}_{\text{aq}}$ quickly reduced $\text{Cu}^{\text{II}}/\text{L}_{\text{org}}$ and pathway A should be favorite, as in the case of $\text{Cu}^{\text{I}}/\text{TPMA}_{\text{aq}}$. Conversely, if $E_{1/2} > 0$, $\text{Cu}^{\text{I}}/\text{L}_{\text{aq}}$ did not efficiently reduce $\text{Cu}^{\text{II}}/\text{L}_{\text{org}}$ but persisted in the organic phase in order to preferentially activate $\text{P}_n\text{-X}$ (pathway B). The less reactive $\text{Cu}^{\text{II}}/\text{bpy}_{\text{aq}}$ should follow this second pathway, whereas $\text{Cu}^{\text{II}}/\text{BPMEA}_{\text{aq}}$ may be involved in both pathways A and B. Activation of R-X is typically a slow reaction due to the negative reduction potential of R-X and the high energy involved in the C-X bond breaking.^{84,117}

Regarding radical deactivation, reaction with $\text{X-Cu}^{\text{II}}/\text{L}_{\text{org}}$ was the major pathway for every dual catalytic system because in the absence of $\text{X-Cu}^{\text{II}}/\text{L}_{\text{org}}$ the reaction was not controlled for the lack of deactivators in the oil phase (Table 4, entries 4 and 5). Therefore, the ultimate result of both catalytic cycles in Scheme 2 was the reduction of $\text{X-Cu}^{\text{II}}/\text{L}_{\text{org}}$ by $\text{Cu}^{\text{I}}/\text{L}_{\text{aq}}$, either direct (pathway A) or mediated by the ATRP reaction (pathway B).

$\text{X-Cu}^{\text{II}}/\text{L}_{\text{org}}$ resulting from termination reactions (see Scheme 1) was reduced back to $\text{Cu}^{\text{I}}/\text{L}_{\text{org}}$ by the continuous supply of electrogenerated $\text{Cu}^{\text{I}}/\text{L}_{\text{aq}}$ (reaction 1). This allowed for the use of a relatively low catalyst loading (1000 ppm of oil-soluble copper complex). Catalyst regeneration was confirmed by analysis of the consumed electrical charge during *e*ATRP. The theoretical charge to completely reduce the dual catalyst from Cu^{II} to Cu^{I} was 9.2 C, while in most cases a higher current was consumed (Table 4), indicating catalyst regeneration. However, a lower charge was expended when using $\text{Cu}^{\text{II}}/\text{TPMA}_{\text{aq}}$, the most hydrophilic of the tested catalysts; electrogenerated $\text{Cu}^{\text{I}}/\text{TPMA}_{\text{aq}}$ slowly migrated to the organic phase to reduce $\text{Cu}^{\text{II}}/\text{L}_{\text{org}}$, resulting in weak electrocatalysis.

Overall, rate and efficiency of miniemulsion *e*ATRP were regulated by the hydrophobicity of the aqueous phase catalyst, which in turn affected catalyst partition. This represented a new way to modulate catalyst activity in ATRP, different from the traditional activity trends based on the redox potential of the Cu complexes.

Effects of E_{app} on Kinetics of Miniemulsion *e*ATRP

Polymerization rate could be modulated by changing the energy of the electrode|water interface, which could be simply achieved by changing E_{app} . Thus, a series of miniemulsion polymerizations were carried out at different E_{app} with a suitable dual catalyst combination ($\text{Cu}^{\text{II}}/\text{BPMEA}_{\text{aq}} + \text{Cu}^{\text{II}}/\text{BPMODA}^*_{\text{org}}$). E_{app} was selected from the reversible CV recorded in the polymerization mixture (Figure 5 and Table 5, entries 1–3). For each of the three selected values of E_{app} , M_n increased linearly with monomer conversion and matched well the theoretical values ($M_{n,\text{th}}$). A narrow MWD was obtained, indicating uniform growth of polymer chains. As expected, more reducing conditions resulted in an increased ATRP rate: k_p^{app} gradually increased with decreasing E^{app} ($k_p^{\text{app}} = 0.035, 0.036, \text{ and } 0.041 \text{ h}^{-1}$ for $E_{1/2}$, E_{pc} , and $E_{\text{pc}} - 80 \text{ mV}$, respectively, Figure S13). The most reducing conditions led to the highest monomer conversion after 24 h (71% at $E_{\text{app}} = E_{\text{pc}} - 80 \text{ mV}$, approximately the mass transport limit for $\text{CuBr}_2/\text{L}_{\text{aq}}$ reduction).⁸⁸ However, changing E_{app} had less effect on k_{app} than changing catalyst combination.

Different Targeted DP

To test the versatility of miniemulsions *e*ATRP with $\text{Cu}^{\text{II}}/\text{BPMEA}_{\text{aq}} + \text{Cu}^{\text{II}}/\text{BPMODA}^*_{\text{org}}$, polymerizations with different target DP were carried out by varying the amount of initiator (at $E_{\text{app}} = E_{\text{pc}}$, Table 5, entries 2 and 4–6). Polymerizations showed almost linear first-order kinetics, M_n matching the theoretical values, and low PDI (Figure 6). In each case, GPC traces showed a clear peak shift from low to high molar mass (Figure S14). The polymerization rate (eq 1) increased with the concentration of initiator, and the lowest target DP showed the highest k_p^{app} ($[\text{M}]/[\text{R-X}] = 150$, Figure 6A). Conveniently, for $[\text{M}]/[\text{R-X}] = 500$, k_p^{app} could be enhanced by applying a more negative E_{app} , maintaining a similar level of polymerization control and thus confirming the versatility of *e*ATRP under miniemulsion conditions (Table 5, entries 4 and 5).

3. CONCLUSION

An electrochemical approach was successfully applied to mediate ATRP in dispersed media (miniemulsion). Well-controlled *e*ATRP of BA was achieved using a dual catalyst system, i.e., a combination of two different copper catalysts ($\text{Cu}^{\text{II}}/\text{L}_{\text{aq}} + \text{Cu}^{\text{II}}/\text{L}_{\text{org}}$). First, $\text{Cu}^{\text{II}}/\text{L}_{\text{aq}}$ was reduced at the electrode|water interface. Then, the electrochemical stimulus was shuttled from electrode via water to the organic phase droplets mainly by migration of $\text{Cu}^{\text{I}}/\text{L}_{\text{aq}}$. Analysis of the polymerization rate with different catalyst combinations indicated that interfacial ET between $\text{Cu}^{\text{I}}/\text{L}_{\text{aq}}$ and $\text{Cu}^{\text{II}}/\text{L}_{\text{org}}$ was negligible. The dual mediator system was not perfectly compartmentalized, but there was a dynamic exchange between the two liquid phases: $\text{Cu}^{\text{I}}/\text{L}_{\text{aq}}$ migrated toward the organic phase, and $\text{Cu}^{\text{II}}/\text{L}_{\text{aq}}$ migrated back the aqueous phase, closing the heterogeneous electrochemical cycle.

Selection of the proper catalysts combination was necessary to obtain fast and controlled miniemulsion *e*ATRP. The best polymerization results were obtained with $\text{CuBr}^2/\text{BPMEA}_{\text{aq}} + \text{CuBr}^2/\text{BPMODA}^*_{\text{org}}$, which produced stable latexes and well-defined polymers with different DP.

Reaction rate could be enhanced and modulated by changing E_{app} (i.e., by changing the energy of the electrode|water interface). However, hydrophobicity and partition coefficient of $\text{Cu}^{\text{II}}/\text{L}_{\text{aq}}$ were the most important parameters to modulate both rate and control of the heterogeneous polymerization. This finding diverges from traditional ATRP systems, which are predominantly regulated by the redox properties of the catalyst. In miniemulsion *e*ATRP, catalyst partition and interfacial dynamics are new important parameters to regulate the process.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Structure of the investigated ligands to form hydrophilic (A) and hydrophobic (B) copper complexes.

Figure 2.

(A) Hydrophobicity/hydrophilicity of the catalysts based on their distribution in BA/water (15% v/v) at 60 °C (Table 1). (B) Electrochemical reactivity of the catalysts based on $CuBr_2/L$ half-wave potential in BA/anisole 1/1 (v/v) (the thicker the arrow, the stronger the reducing agent). (C) Activity of the aqueous phase catalysts based on k_p^{app} during miniemulsion eATRP with $CuBr_2/BPMODA$ (left) or $CuBr_2/BPMODA^*$ (right) as organic phase catalyst. ■ = aqueous phase catalyst; ● = organic phase catalyst.

Figure 3.

(A) CV of 2 mM $\text{CuBr}_2/\text{L}_{\text{aq}}$ complexes in water + 0.1 M NaBr. (B) CV of 1 mM $\text{CuBr}_2/\text{L}_{\text{aq}}$ + 1.4 mM $\text{CuBr}_2/\text{BOMODA}^*$ in miniemulsion in the presence of 4.9 mM EBiB, recorded on Pt disk electrode at $\nu = 0.1 \text{ V s}^{-1}$ and $T = 60^\circ \text{C}$ (concentrations referred to V_{tot}). The black circles represent E_{app} during each eATRP.

Figure 4.

(A) Logarithmic kinetic plot and (B) MW and evolution vs monomer conversion for the miniemulsion *e*ATRP with Cu^{II}/BPMDA*_{org} and different Cu^{II}/L_{aq}. (C) GPC traces obtained during *e*ATRP with the BPMEA_{aq}–BPMDA_{oil} ligand combination (Table 4, entry 10).

Figure 5.

Effect of E_{app} on BA miniemulsion polymerization. (A) CV of 1 mM $CuBr_2$ /BPMEA + 1.4 mM $CuBr_2$ /BPMODA* in miniemulsion. The circles correspond to the selected E_{app} during eATRP. (B) MW and evolution vs conversion. (C, D) GPC trace with various E_{app} s.

Figure 6. Miniemulsion eATRP with different target DP. (A) Kinetic plot and (B) M_n and M_w/M_n vs monomer conversion.

Scheme 1.
Mechanisms of ATRP and eATRP

Scheme 2.

Proposed Mechanism of Miniemulsion Polymerization by eATRP (Coordination of X^- to Cu^{II}/L Was Omitted for Simplicity)

Table 1Partition of CuBr₂/L Catalysts between Water and BA^a

L	[CuBr ₂ /L] _{water} /[CuBr ₂ /L] _{tot}			
	15 vol % BA ^b		30 vol % BA ^c	
	RT	60 °C	RT	60 °C
BPMODA	N/A	N/A	0.30	N/A
BPMODA* ^d	N/A	N/A	0.10	0.31
BPMEA	0.54	0.88	0.73	0.98
bpy	0.71	0.93	0.84	0.98
TPMA	1.00	1.04	1.00	1.00

^a[CuBr₂/L]_{tot} = 2.5 mM. Ratios of [CuBr₂/L]_{water}/[CuBr₂/L]_{tot} were determined by calibration curve in water (Figures S1 and S2).

^b13.5 wt % of BA.

^c27.8 wt % of BA.

^dFrom ref 106.

Table 2Half-Wave Potentials of CuBr₂/L at 60 °C^a

L	<i>E</i> _{1/2} (V vs SCE)		
	aq phase ^b	miniemulsion ^c	org phase ^d
TPMA	−0.311	−0.235	−0.188
BPMEA	−0.256	−0.114	−0.004
bpy	−0.091	0.085	0.247
BPMODA*	N/A ^e	N/A ^f	−0.132
BPMODA	N/A ^e	N/A ^f	−0.040

^a Recorded on a Pt disk electrode at a scan rate of 0.1 V s^{−1}.^b Water + 0.1 M NaBr.^c Miniemulsion without EBiB (both aqueous phase catalyst and Cu^{II}/BPMODA* were present).^d BA/anisole 1/1 (v/v) + 0.1 M Et₄NPF₆.^e Insoluble in water.^f Electrochemical faradaic signal was too small to reliably measure *E*_{1/2}.

Table 3Composition of Organic and Aqueous Phases in a Typical Miniemulsion Polymerization^a

component	weight (g)	comments
organic phase		
BA	7.15	20 vol % (18 wt %) to total
EBiB	0.038 ^b	[BA]/[EBiB] = 283/1
HD	0.39	5.4 wt % to BA
CuBr ₂ /BPMODA ^c	0.012/0.024	[CuBr ₂]/[BPMODA] = 1/1; 1000 ppm to monomer; 1.4 mM with respect to V_{tot}
aqueous phase		
water	32	distilled water
SDS	0.33	4.6 wt % to BA
NaBr	0.41	[NaBr] = 0.1 M
CuBr ₂ /BPMEA ^d	8.9×10^{-3} /0.010	[CuBr ₂]/[BPMEA] = 1/1; 1 mM with respect to V_{tot}

^aPolymerization conditions: $T = 60\text{ }^{\circ}\text{C}$; WE = Pt mesh; CE = Pt mesh (separated from reaction mixtures methylated cellulose gel saturated with supporting electrolyte); RE = Ag/AgI/I[−].

^bAmount of EBiB was varied depending on target degree of polymerization (DP).

^cCuBr₂/BPMODA* was also used as organic phase catalyst.

^dCuBr₂/bpy and CuBr₂/TPMA were also used as aqueous phase catalysts.

Table 4

eATRP of BA in Miniemulsion with Different Catalyst Combinations at $T = 60\text{ }^{\circ}\text{C}^a$

entry	L_{aq}^b	L_{org}^c	$E_{1/2}^d$ (V)	E_{app}^e	t (h)	Q^f (C)	conv ^g (%)	$k_p^{\text{app}} h$ (h ⁻¹)	M_n^i	M_{th}^j	i
1	BPMEA	BPMODA	-0.036	-	24	0	0	-	-	-	-
2	-	BPMODA	-	$-k$	24	0.9	7	0.004	20000	2600	1.92
3	-	BPMODA*	-	$-k$	24	0.6	5	0.003	19300	2100	1.67
4	bpy	-	-	E_{pc}	10	1.9	54	0.101	12100	19800	9.31
5	BPMEA	-	-	E_{pc}	24	2.0	66	0.062	29100	24300	4.62
6	bpy	BPMODA	-0.287	E_{pc}	22	14.0	30	0.016	13300	11100	1.78
7	BPMEA	BPMODA	-0.036	E_{pc}	24	13.4	94	0.108	31600	34300	1.50
8	TPMA	BPMODA	0.148	E_{pc}	24	7.9	17	0.007	8200	6400	2.53
9	bpy	BPMODA*	-0.379	E_{pc}	24	12.3	57	0.037	20900	20900	1.26
10	BPMEA	BPMODA*	-0.128	E_{pc}	24	11.2	68	0.048	27400	24900	1.19
11	TPMA	BPMODA*	0.056	E_{pc}	24	6.6	13	0.006	12400	5100	1.32

^aPolymerization conditions as described in Table 3, with [BA]/[EBiB] = 283/1.^bLigand used to prepare the aqueous phase catalyst.^cLigand used to prepare the organic phase catalyst.^d $\Delta E_{1/2} = E_{\text{Cu}^{\text{II}}L_{\text{org}}^{\text{I}}/\text{Cu}^{\text{I}}L_{\text{org}}^{\text{I}}} - E_{\text{Cu}^{\text{II}}L_{\text{aq}}^{\text{I}}/\text{Cu}^{\text{I}}L_{\text{aq}}^{\text{I}}}$, calculated from the values in Table 2.^eSelected from CV response (e.g., Figure 3B).^fDetermined from the chronoamperometry recorded during electrolysis.^gDetermined by gravimetric analysis.^hThe slope of the $\ln([M]_0/[M])$ vs time plot.ⁱDetermined by THF GPC with polystyrene standards.^j $M_{\text{th}} = [M]/[\text{EBiB}] \times \text{MW}_M \times \text{conversion} + \text{MMEBiB}$.^kSince a clear voltammetric peak was not detected, an arbitrary $E_{\text{app}} = -0.3\text{ V}$ vs SCE was applied, a value sufficiently negative to oxidize all present copper species.

Table 5eATRP of BA in Miniemulsion at Different E_{app} and Target DP at $T = 60\text{ }^{\circ}\text{C}^a$

entry	[M]/[R-X]	E_{app}^b	Q^c (C)	conv ^d (%)	k_{app}^e (h ⁻¹)	$M_{n,\text{GPC}}^f$	$M_{n,\text{th}}^g$	f
1	283/1	$E_{1/2}$	3.0	55	0.035	21100	20100	1.24
2	283/1	E_{pc}	11.2	68	0.036	27400	24900	1.19
3	283/1	$E_{\text{pc}} - 80\text{ mV}$	3.7	71	0.041	31700	25900	1.19
4	150/1	E_{pc}	9.6	53	0.117	17100	18300	1.29
5	500/1	E_{pc}	4.9	28	0.014	21200	18100	1.26
6	500/1	$E_{\text{pc}} - 80\text{ mV}$	20.5	79	0.074	54000	50700	1.30

^a Polymerization conditions as described in Table 3.^b Selected from CV (e.g., Figure 3B).^c Determined from the chronoamperometry recorded during electrolysis.^d Determined by gravimetric analysis.^e The slope of the $\ln([M]_0/[M])$ vs time plot.^f Determined by THF GPC with polystyrene standards.^g $M_{n,\text{th}} = [M]/[EBiB] \times MM[M] \times \text{conversion} + MMEBiB$.