PEO-*b*-PNIPAM Copolymers via SARA ATRP and *e*ATRP in Aqueous Media

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ABSTRACT

Supplemental activator and reducing agent atom transfer radical polymerization (SARA ATRP) and electrochemically mediated atom transfer radical polymerization (*e*ATRP) of *N*-isopropylacrylamide were investigated in aqueous media. The synthesis of poly(ethylene oxide)-*block*-poly(*N*-isopropylacrylamide) copolymers *via* SARA ATRP was carried out, utilizing 500 ppm of Cu^{II} species, rather than previously reported *ca.* 2,500-50,000 ppm of Cu^I/L used to pre-disproportionate in situ to form Cu⁰ and Cu^{II}/L. The copolymers were also prepared *via e*ATRP under potentiostatic conditions. Various polymerization parameters were examined including the effect of the targeted degree of polymerization (DP) and, in the case of SARA ATRP, the influence of copper surface area on the polymerization. Under optimized reaction conditions, the DP of resulting copolymers increased linearly with monomer conversion. Successful formation of the block copolymers confirmed the living nature of the polymers prepared by SARA ATRP and *e*ATRP of *N*-isopropylacrylamide in aqueous media.

KEYWORDS

aqueous media, *N*-isopropylacrylamide copolymers, electrochemically mediated ATRP, SARA ATRP, controlled radical polymerization

INTRODUCTION

Atom transfer radical polymerization (ATRP) is one of the most often used reversible deactivation radical polymerization (RDRP) methods, allowing effective control over polymer molecular weight (MW), generating (co)polymers with narrow molecular weight distribution (MWD), site selected functionalities, controlled architectures, and well-defined compositions.[1-7] Monomers with various functionalities have been successfully polymerized by ATRP, including various styrenes, acrylates, methacrylates, acrylamides, and acrylonitrile as well as vinyl pyridine.[6-10]

Poly(*N*-isopropylacrylamide) (PNIPAM) is widely used in cosmetics, for biomedical applications, wastewater treatment, and oil recovery.[11, 12] However, successful ATRP of acrylamides and its derivatives may be challenging with respect to the control of the polymerization when using water as the solvent. ATRP of NIPAM has relatively low value of ATRP equilibrium constant (K_{ATRP}) and some potential side reactions that include ligand displacement from the copper catalyst by the formed polymers, and loss of chain-end halogen (C-X) by solvolysis.[6] Since the $\text{X-Cu}^{\text{II}}/\text{L}$ bond can easily dissociate in aqueous media, typically high concentration of catalyst is needed, or the presence of salts with halide anions is required.[13, 14] Hydrolysis of alkyl halides in water can be suppressed by conducting the polymerizations at lower temperatures.[12, 15, 16] The best control over an ATRP of (meth)acrylamides was obtained using one of the most active catalytic systems $\text{Cu}^{\text{I}}\text{Br}/\text{Me}_6\text{TREN}$ (Me_6TREN = tris(2-(dimethylamino)ethyl)amine) due to its intrinsically high values for K_{ATRP} . [2, 17] PNIPAM with narrow MWD ($M_w/M_n = 1.08$) was prepared by employing water soluble initiator, however high catalyst loadings (*ca.* 10,000-15,000 ppm) were used.[15]

Recently another procedure for synthesis of PNIPAM with narrow MWD ($M_w/M_n = 1.13-1.22$) was reported, but it typically required a large amount of organic solvent, at least 50%. [18, 19] NIPAM copolymers with poly(ethylene oxide) were reported, however the polymerizations either took long time (24 h) to reach high conversion and yielded polymers with broad MWD ($M_w/M_n = 1.45-1.51$), [20] required the use of high amounts of organic (co)solvent, [21] or high amounts of catalyst. [22]

The development of new ATRP systems, utilizing parts per million (ppm) concentrations of catalyst, can provide well-controlled polymerizations of various monomers using highly active copper catalysts under more environmentally benign and industrially scalable reaction conditions. [6, 23] These methods allow for significant reduction of the amount of catalyst used due to continuous regeneration of the $\text{Cu}^{\text{I}}/\text{L}$ activator complex from excess $\text{Cu}^{\text{II}}/\text{L}$ deactivator species. This can be achieved either by employing chemical reducing agents such as glucose, [24] ascorbic acid, [25] sulfites, [26] hydrazine, [27] Sn^{II} compounds [28, 29] or silver metal [30] in a process termed activators regenerated by electron transfer (ARGET) ATRP, [28, 31] conventional thermal free radical initiators (*e.g.*, azo-initiators) in initiators for continuous activator regeneration (ICAR) ATRP, [27, 32] zerovalent metals including Cu^0 in supplemental activator and reducing agent (SARA) ATRP, [14, 33-38] photochemical reduction of the $\text{Cu}^{\text{II}}/\text{L}$ complex in photoATRP, [23, 39] or by applying a reducing potential in electrochemically mediated ATRP (*e*ATRP). [10, 40-46]

Among these low ppm Cu ATRP methods, SARA ATRP offers simple removal and reuse of unreacted Cu^0 and control over the polymerization rate (R_p) by the surface area of Cu^0 . [14, 34, 35, 37] On the other hand, *e*ATRP stands out due to the possibility of

recycling/reusing the transition metal (*e.g.*, copper), in addition to facile control over the polymerization rate and the ability to intermittently switch a polymerization between “on” and “off” states.[40, 42]

In addition to the ATRP equilibrium between Cu^{I} and Cu^{II} species, SARA ATRP employs a zerovalent metal, which introduces additional slow reactions, *i.e.* supplemental activation of alkyl halides by Cu^0 and reduction of $\text{Cu}^{\text{II}}/\text{L}$ back to $\text{Cu}^{\text{I}}/\text{L}$ through comproportionation, as well as kinetically negligible disproportionation of $\text{Cu}^{\text{I}}/\text{L}$ (**Scheme 1**). SARA ATRP is also termed as single electron transfer living radical polymerization (SET-LRP).[47] Recent mechanistic studies[48-50] have shown that the mechanism of RDRP in the presence of Cu^0 is consistent with SARA ATRP in dimethyl sulfoxide (DMSO), acetonitrile (MeCN) or even in water with Me_6TREN or tris(2-pyridylmethyl)amine (TPMA).[14]

Scheme 1. Mechanism of SARA ATRP. Line thickness denotes the contributions of the reactions (bold: major reactions, solid: contributing reactions, dashed: negligible reactions). The radical products of activation reactions, alkyl halide products of deactivation reactions, and stoichiometric balance are omitted for clarity. Cu^0 , $\text{Cu}^{\text{I}}\text{X}/\text{L}$ and $\text{Cu}^{\text{II}}\text{X}_2/\text{L}$ represent all Cu^0 , Cu^{I} and Cu^{II} species, respectively, without particular speciation. Reproduced from ref. [35] with permission from The Royal Society of Chemistry.

In *e*ATRP, the ratio of $\text{Cu}^{\text{I}}/\text{L}$ to $\text{X-Cu}^{\text{II}}/\text{L}$ concentration is precisely controlled by applied current (I), potential (E), and total charge passed (Q) at the electrode surface.[41, 42] The activator reduced by electrolysis is then distributed through the reaction mixture by vigorous stirring, and reacts with initiators ($\text{P}_n\text{-X}$) to form radical species ($\text{P}_n^\bullet$) and the oxidized catalyst deactivator ($\text{X-Cu}^{\text{II}}/\text{L}$). Consequently, the radical species propagate to form polymeric chains by reacting with monomers (M), and/or are converted back to a dormant species ($\text{P}_n\text{-X}$) (**Scheme 2**).[10] This allows for fast and controlled polymerizations and synthesis of polymers with complex architectures.[7, 41-45, 51, 52]

Scheme 2. Mechanism of *e*ATRP. Reprinted with permission from.[42] Copyright 2013 American Chemical Society.

This paper is focused on aqueous SARA ATRP and *e*ATRP of *N*-isopropylacrylamide. Polymerization conditions were optimized to provide for fast reactions employing low catalyst concentrations, while maintaining narrow molecular weight distributions. Successful preparation of poly(ethylene oxide)-*block*-poly(*N*-isopropylacrylamide) (PEO-*b*-PNIPAM) diblock copolymers (**Scheme 3**) is reported.

Scheme 3. Synthesis of PEO-*b*-PNIPAM diblock copolymers *via* SARA ATRP or *e*ATRP.

RESULTS AND DISCUSSION

Well-controlled ATRP in aqueous media is challenging due to high values of K_{ATRP} and inefficient deactivation caused by a high degree of reversible dissociation of halide anion from the $\text{X-Cu}^{\text{II}}/\text{L}$ deactivator. Control may be additionally impaired by loss of halide chain end functionality due to elimination or substitution reactions in aqueous media or in the presence of monomers with nucleophilic groups.[12, 13, 15, 53] Typically, high catalyst loadings are required to compensate for the side reactions. However, it has been shown that concentration of catalyst employed in aqueous media can be substantially diminished when salts with halide anions are introduced.[14] Thus, the objective of this study was to investigate and optimize polymerization conditions for ATRP of NIPAM using poly(ethylene oxide) macroinitiators (PEO MI, $M_n = 2000$, $M_w/M_n = 1.16$), resulting in formation of PEO-*b*-PNIPAM block copolymers.

Since $\text{Cu}^{\text{I}}\text{X}/\text{Me}_6\text{TREN}$ complexes undergo almost complete disproportionation in pure water, the recently reported ATRP in aqueous media were attributed to the SET-LRP mechanism.[12] However, in the presence of alkyl halides, required for

polymerization, disproportionation is kinetically minimized.[50] Motivated by a very good control over the polymerization in aqueous media with high Cu amounts (*ca.* 2,500-50,000 ppm of Cu^I/L pre-disproportionated to form Cu⁰ and Cu^{II}/L complexes), we aimed to achieve similar control but using only 500 ppm of Cu^{II}/L in solution, following the SARA ATRP mechanism. In addition, *e*ATRP under potentiostatic conditions (applied constant potential) with a conventional three electrode system – a platinum (Pt) mesh working electrode, a Pt mesh counter electrode (separation from the reaction media using methylated cellulose gel), and a Ag/AgI/T reference electrode was studied.

In SARA ATRP, a range of polymerization parameters was examined, such as targeted degree of polymerization (DP) and surface area of copper. Results are summarized in **Table 1**.

Table 1. Summary of PNIPAM and PEO-*b*-PNIPAM synthesis by SARA ATRP and *e*ATRP.

entry	time	[NIPAM]/[I]/[Cu ^I Br]/	<i>S/V</i>	<i>k_p</i> ^{app}	conv	<i>M_{n,theo}</i>	<i>M_n</i> ^{app}	<i>M_w/M_n</i> ^d
	(h)	[Cu ^{II} Br ₂ /2Me ₆ TREN]	(cm ⁻¹) ^a	(h ⁻¹) ^b	(%) ^b	(×10 ⁻³) ^c	(×10 ⁻³) ^b	
1	2	200 / 1 ^e / 0.1 / 0.9	–	1.294	92	21.0	20.0	1.18
2	2	200 / 1 ^f / 0.1 / 0.9	–	0.951	86	21.6	20.8	1.17
3	2	10 / 1 ^e / 0 / 0.005	0.68	1.017	90	1.2	1.2	1.07
4	12	100 / 1 ^e / 0 / 0.05	0.68	0.303	81	9.3	9.8	1.15
5	21	200 / 1 ^e / 0 / 0.1	0.68	0.137	52	12.0	11.7	1.29
6	21	200 / 1 ^f / 0 / 0.1	0.16	0.077	43	11.8	11.1	1.28
7	21	200 / 1 ^f / 0 / 0.1	0.34	0.096	49	13.2	11.8	1.28
8	21	200 / 1 ^f / 0 / 0.1	1.20	0.229	70	17.9	19.5	1.24
9	21	200 / 1 ^f / 0 / 0.1	2.06	0.302	75	19.0	21.2	1.19

10	1	200 / 1 ^f / 0 / 0.1	–	3.885	95	23.6	24.5	1.18
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ATRP: entries 1–2; SARA ATRP: entries 3–9; eATRP: entry 10. General reaction conditions: $T = 0\text{ }^{\circ}\text{C}$; $V_{\text{tot}} = 8\text{ mL}$ (in $\text{H}_2\text{O}/\text{DMF} = 9/1$ by v/v) (except entry 6–10, $V_{\text{tot}} = 33\text{ mL}$); $[\text{I}]_0 = 4.1\text{ mM}$ (except entry 3: $[\text{I}]_0 = 82.0\text{ mM}$ and entry 4: $[\text{I}]_0 = 8.2\text{ mM}$); $[\text{NIPAM}]_0 = 0.8\text{ M}$; Supporting electrolyte concentration (tetraethylammonium bromide, TEABr) = 0.1 M . ^aRatio of surface area (S) of Cu^0 to total volume of reaction mixture (V); ^bMonomer conversion, apparent M_n and k_p were determined by ^1H NMR; ^c $M_{n,\text{theo}} = ([\text{M}]_0/[\text{I}]_0) \times \text{conversion} \times M_{\text{monomer}} + M_{\text{initiator}}$; ^dMWD was determined by DMF GPC with PEO standards; ^eI = hydroxyethyl α -bromoisobutyrate (HEBiB); ^fI = poly(ethylene oxide) macroinitiators, PEO MI; In case of entry 10: $E_{\text{app}} = E_{\text{pc}} - 120\text{ mV}$ (vs. $\text{Ag}/\text{AgI}/\text{I}^-$); Working electrode = Pt mesh; Counter electrode = Pt mesh (separated from the reaction solution by the supporting electrolyte saturated Tylose gel ($\text{MH} = 300$)); Reference electrode = $\text{Ag}/\text{AgI}/\text{I}^-$.

Homopolymerization and block copolymerization of NIPAM was conducted *via* ATRP with high concentration (5000 ppm) of Cu catalyst (**Table 1, entries 1-2 and Figures S3a-b, S4a-b**). The majority of Cu was introduced in the form of deactivator complex in order to slow down otherwise very rapid polymerization. Even with just 10% of the catalyst in the lower oxidation state the polymerizations were fast, reaching 92% and 86% monomer conversion after 2 h, for the homopolymerization and block copolymerization, respectively. The substantial amount of Cu catalyst diminished the effect of side reactions such as reversible dissociation of halide anion from the deactivator complex, resulting in well controlled polymers.

Effect of Targeted Degree of Polymerization. The effect of initial molar ratio of NIPAM monomer to initiator on the homopolymerization was investigated in the presence of $\text{Cu}^{\text{II}}\text{Br}_2/\text{Me}_6\text{TREN}$ catalyst complex as reported in **Table 1, entries 3–5**,

Figure 1a,b, and S5a-c. Well controlled polymers were synthesized using aqueous SARA ATRP in the presence of Cu^0 (powder; $S/V = 0.68 \text{ cm}^{-1}$) with 500 ppm of $\text{Cu}^{\text{I}}/\text{L}$, in the presence of an excess of bromide salt, $[\text{TEABr}]_0 = 0.1 \text{ M}$. This concentration of Cu/L species generates essentially transparent, colorless solutions and represents a 5-100 fold reduction in Cu/L relative to previous reports of *ca.* 2,500-50,000 ppm $\text{Cu}^{\text{I}}/\text{L}$ used for pre-disproportionation in water.[12, 54] Polymerizations were performed at three different ratios of $[\text{M}]_0/[\text{I}]_0 = 10, 100$ and 200 , targeting different DP. The apparent propagation constant (k_p^{app}) was measured at initial time periods. The rate of polymerization (R_p), defined as $R_p = k_p[\text{M}][\text{P}\cdot] = k_p[\text{M}]K_{\text{ATRP}} \frac{[\text{P-X}][\text{Cu}^{\text{I}}/\text{L}]}{[\text{X-Cu}^{\text{II}}/\text{L}]}$, followed the first order with respect to P-X concentration. Values of k_p^{app} increased approximately linearly with $[\text{I}]_0$ (**Figure 1a, Figure S6**). MW evolutions were well-matched with the theoretical values (**Figure 1b**) and maintained narrow MWD (**Figure S5a-c**). Significantly higher k_p^{app} and monomer conversion of $>90\%$ were obtained for polymerizations carried out at higher concentration of initiator (*e.g.*, $[\text{M}]_0/[\text{I}]_0 = 10$). Polymerizations were faster than at lower concentration of $[\text{I}]_0$, compare k_p^{app} ; **Table 1, entries 3 vs. 4–5**.

Figure 1. SARA ATRP of NIPAM as a function of targeted DP (10, 100 and 200). (a) First-order kinetic plot of monomer conversion versus time, and (b) M_n and M_w/M_n versus monomer conversion. Reaction conditions: $[NIPAM]_0 = 0.8$ M, ■ $[NIPAM]/[HEBiB] = 10/1$, ▼ $[NIPAM]/[HEBiB] = 100/1$ or ● $[NIPAM]/[HEBiB] = 200/1$, $[Cu^{II}Br_2]_0 = 0.41$ mM (500 ppm), $[Me_6TREN]_0 = 0.82$ mM, $T = 0$ °C, $[TEABr]_0 = 0.1$ M, Cu^0 powder ($S/V = 0.68$ cm⁻¹), $V_{tot} = 8$ mL.

Influence of the surface area of Cu to solution volume ratio (S/V). Since Cu^0 in the form of a powder (**Table 1, entries 6–7**) or a sponge (**Table 1, entries 8–9**) acts predominantly as a supplemental, rather than the major activator of alkyl halides,[35] four separate experiments were conducted with varying amounts of Cu^0 surface area to solution volume ratio, $S/V = 0.16, 0.34, 1.20$, and 2.06 cm⁻¹, respectively (**Figure 2a,b and S5d-g**). **Figure 2** illustrates the polymerization kinetics and molecular weight evolution with conversion. As the surface area of Cu^0 was decreased, S/V from 2.06 cm⁻¹ to 0.16 cm⁻¹; **Table 1, entries 6–9**, the rate of polymerization similarly declined, k_p^{app} from 0.302 h⁻¹ to 0.077 h⁻¹, compare k_p^{app} ; **Table 1, entries 6–9**, suggesting the involvement of Cu^0 in the rate-determining step of the reaction, following equation: $R_a = k_p^{app} \left(\frac{S}{V} \right) [I]$. [14] Molecular weights increased linearly with conversion (**Figure 2b**), and were nearly identical to theoretical values. Molecular weight distributions were independent of copper surface area and remained low, with $MWD = 1.19$ at 75% monomer conversion ($S/V = 2.06$ cm⁻¹). Since reaction rate depends on the Cu^0 surface area to reaction volume ratio (S/V) and not on absolute amount of copper used, reaction rate could be feasibly increased by either increasing the surface area of metallic copper or decreasing total reaction volume. A linear relationship between the k_p^{app} and the square root of (S/V) was observed (**Figure S7**).[55]

Figure 2. SARA ATRP of NIPAM as a function of the ratio of surface area of Cu^0 to total volume of reaction mixture ($S/V = 0.16, 0.34, 1.20$, and 2.06 cm^{-1}). (a) First-order kinetic plot of monomer conversion versus time, and (b) M_n and M_w/M_n versus monomer conversion. Reaction conditions: $[\text{NIPAM}]/[\text{PEO MI}]/[\text{Cu}^{\text{II}}\text{Br}_2]/[\text{Me}_6\text{TREN}] = 200/1/0.1/0.2$, $[\text{CuBr}_2]_0 = 0.4 \text{ mM}$ (500 ppm), $[\text{NIPAM}]_0 = 0.8 \text{ M}$, $T = 0 \text{ }^\circ\text{C}$, $[\text{TEABr}]_0 = 0.1 \text{ M}$, $V_{\text{tot}} = 33 \text{ mL}$.

Electrochemically mediated ATRP of NIPAM. The series of experiments explored $e\text{ATRP}$ of NIPAM under standard polymerization conditions ($\text{Cu}^{\text{II}}\text{Br}_2/\text{Me}_6\text{TREN}$, $\text{DP} = 200$, and $T = 0 \text{ }^\circ\text{C}$) (**Figure 3a-c and S8a,b**). $E_{1/2}$ values for $\text{Cu}^{\text{II}}\text{Br}_2/\text{Me}_6\text{TREN}$ complex are reported in the Supporting Information (**Figure S8a**), conducted in the absence and presence of a PEO MI. The CV response of $\text{X-Cu}^{\text{II}}/\text{L}$ drastically changed when the initiator was added; the cathodic peak approximately doubled in height while the anodic one decreased, clearly indicating that $\text{Cu}^{\text{I}}/\text{L}$ rapidly reacted with PEO MI. The applied potential (E_{app}) was selected as $E_{\text{app}} = E_{\text{pc}} - 120 \text{ mV}$ and polymerization was carried out under potentiostatic conditions. Polymerization was up to 40 times faster (compare k_p^{app} ; **Table 1, entries 6–9 vs. 10**) than for SARA ATRP with Cu^0 . The MWD of the second block can be determined using the following

equation: $Y_{\text{PEO-PNIPAM}} = w_{\text{PEO}}^2 Y_{\text{PEO}} + w_{\text{PNIPAM}}^2 Y_{\text{PNIPAM}}$, where w is weight fraction of each block and $Y = \bar{D} - 1$ [56] (where $\bar{D}$ is defined as dispersity). The weight fraction of PNIPAM was 0.84 (**Table 1, entry 10**) based on monomer consumption. According to this equation, the calculated MWD of PNIPAM block was 1.25, indicating that well-defined polymers were synthesized by *e*ATRP under optimized conditions. In addition, clean shift towards higher molecular weights was observed in GPC, demonstrating efficient chain extension of PEO-MI to a block copolymer.

Figure 3. *e*ATRP of NIPAM. (a) First-order kinetic plot, (b) M_n and M_w/M_n versus monomer conversion, and (c) GPC traces. Reaction conditions: $[\text{NIPAM}]/[\text{PEO-MI}]/[\text{Cu}^{\text{II}}\text{Br}_2]/[\text{Me}_6\text{TREN}] = 200/1/0.1/0.2$,

$[\text{CuBr}_2]_0 = 0.4 \text{ mM}$ (500 ppm), $[\text{NIPAM}]_0 = 0.8 \text{ M}$, $T = 0 \text{ }^\circ\text{C}$, $[\text{TEABr}]_0 = 0.1 \text{ M}$, $V_{\text{tot}} = 33 \text{ mL}$, $E_{\text{app}} = E_{\text{pc}} - 120 \text{ mV}$ (vs. $\text{Ag}/\text{AgI}/\text{I}^-$).

CONCLUSIONS

Both SARA ATRP and *e*ATRP of *N*-isopropylacrylamide was successfully carried out in aqueous media with low catalyst concentration. The synthesis of poly(ethylene oxide)-*block*-poly(*N*-isopropylacrylamide) block copolymers *via e*ATRP (under potentiostatic conditions, 84% wt% of monomer content in H_2O , $0 \text{ }^\circ\text{C}$) or SARA ATRP was efficiently carried out. Effect of targeted degree of polymerization (DP) and influence of surface area of Cu^0 , was studied. Under optimized reaction conditions, the DP of resulting copolymers increased linearly with monomer conversion and semilogarithmic kinetic plots were linear. The successful formation of the block copolymers confirmed the living nature of the *e*ATRP and SARA ATRP of *N*-isopropylacrylamide in aqueous media. Thus, conducting SARA ATRP under appropriate conditions, without pre-disproportionation of $\text{Cu}^{\text{I}}/\text{L}$ complexes and low concentration of Cu species ($[\text{Cu}^{\text{II}}/\text{L}]_0 = 500 \text{ ppm}$), is an efficient synthetic route for functional water-soluble derivatives of acrylamides with controlled chain lengths and narrow molecular weight distributions.

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Associated Content

Supporting Information – Experimental conditions, figures showing determination of Cu⁰ powder and sponge surface area, GPC traces of polymers and CV results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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