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SARA ATRP in Aqueous Solutions Containing Supplemental Redox Intermediate: Controlled Polymerization of [2-(Methacryloyloxy)ethyl] trimethylammonium Chloride

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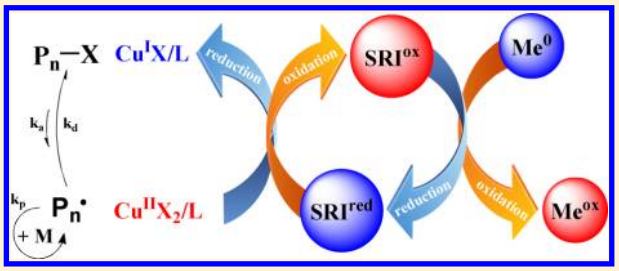
Supporting Information

ABSTRACT: Polymerization of the cationic monomer [2-(methacryloyloxy)ethyl]trimethylammonium chloride (METAC) by the methods of controlled radical polymerization AGET ATRP and SARA ATRP is reported, demonstrating successful synthesis of well-defined cationic polymers in aqueous solutions. A modification of SARA system (ISARA) for aqueous solutions was proposed based on the use of supplemental redox intermediates (SRI) mediating electron transfer between zerovalent metal and the deactivator Cu^{II}/L, ensuring steady generation of the activator *in situ*. Ascorbic acid and hydroquinone in their oxidized form, and iron(III) chloride are between preferable SRI. A mechanism of generation of the activator Cu^{I}/L in the presence of zerovalent metals and SRI in aqueous solutions of ISARA ATRP was proposed. The main advantages of ISARA compared to AGET ATRP are simpler technical implementation, better reproducibility of the results and good control over polymerization up to high conversions of the monomers.



INTRODUCTION

Atom transfer radical polymerization (ATRP) is one of the most popular methods of controlled radical polymerization (CRP), which enables synthesis of a wide spectrum of polymers with control over molecular weight and polydispersity. ATRP relies on reversible reaction of a low-oxidation-state metal complex with an alkyl halide generating radicals and the corresponding high-oxidation-state metal complex with a coordinated halide ligand. The reversible reaction ensures that most of the polymer chains grow at the same time.[1,2]

Normal ATRP is very sensitive to oxygen, however, because of rapid trapping of propagating radicals by oxygen and oxidation of the activator Cu^{I}/L (complex of Cu^{I} with polydentate *N*-based ligand). It was demonstrated by Matyjaszewski et al. that oxygen in ATRP systems can be consumed by adding a sufficient amount of reducing agent, tin(II) 2-ethylhexanoate[3] or ascorbic acid,[4] in a process called activators generated by electron transfer (AGET). In AGET ATRP, the activator Cu^{I}/L is first rapidly oxidized by oxygen to the complex of Cu^{II}/L, and the latter is promptly reduced to the Cu^{I}/L state in the presence of a reducing agent. Unfortunately, it is difficult to estimate the exact amount of a reducing agent. If reducing agent is in an excess, the polymerization control is partly lost because of accumulation of relatively large amount of the activator Cu^{I}/L which leads to uncontrolled polymerization. On the contrary, too small amount of a reducing agent is not sufficient to consume oxygen present in the system what results in inhibition of polymerization. An improvement to the AGET process was achieved by employing a reducing agent that reacts slowly and thus can be in an excess. Under these conditions, activators are continuously regenerated by electron transfer (ARGET), and even parts per million of the catalyst Cu^{II}/L in regard to monomer can lead to successful ATRP.[5,6] ARGET ATRP can tolerate large excess of reducing agents and therefore should be more appropriate for the systems in which oxygen must be scavenged. A choice of reducing agents for AGET/ARGET ATRP is limited, however, by their solubility and/or chemical stability in reaction media. Partial solution of such problems comes with electrochemically mediated ATRP (eATRP), where the activator is generated electrochemically, without introduction of chemical reducing agent.[7]

It was determined recently[8] that some zerovalent metals (copper, iron, zinc, magnesium, etc.) can act as supplemental activators and reducing agents (SARA) in ATRP. At the surface of zerovalent metals, redox reaction between reducing metal and the deactivator Cu^{II}/L takes place. As a result of this reaction, the activator Cu^{I}/L and the ions of a reducing metal are generated. The activator diffuses away from the surface of the metal and triggers polymerization. It was shown[9] that this scheme works well in organic solutions ensuring good control over polymerization.

ATRP in aqueous solutions usually results in polymers with relatively higher polydispersity indicating either poor control or actual loss of control.[10] An increase in water content in reaction media accelerates polymerization reactions. This is attributed to

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better solvation of the copper-based ATRP catalyst which increases concentration of the active radicals and, the same, rate of termination.[11,12] Another complication of ATRP in aqueous solutions is related to the partial dissociation of the deactivator $X-Cu^{II}/L$ to free halide anion X^- and the binary Cu^{II}/L complex. Moreover, Cu^I present in the activator can disproportionate producing zerovalent copper and Cu^{II}. Also, the carbon−halogen bond can hydrolyze leading to the loss of chain-end functionality. To suppress dissociation of the deactivator Cu^{II}/L and disproportionation of the activator Cu^I/L, and retain control in aqueous ATRP, high copper concentrations, low ratio Cu^I/L to Cu^{II}/L, and the use of protic solvents as cosolvents were suggested.[13−16] Recently, new possibilities to retain control of polymerization in aqueous ATRP at low copper concentrations were demonstrated by ARGET and ICAR techniques.[17,18] Livingness of the growing chains and proper ratio Cu^I/L to Cu^{II}/L were maintained by continuous addition of a reducing agent or generation of free-radicals.

A possibility to polymerize cationic monomer 2-[(methacryloyloxy)ethyl]trimethylammonium chloride (METAC) by a method of CRP is of general interest since it enables to prepare cationic polymers of a particular structure, e.g. diblock copolymer surfactants[19,20] or polymer brushes containing cationic "tail".[21,22] Among many techniques of CRP, ATRP is the most compatible with protic solvents and monomers bearing cationic groups. ATRP of METAC in different solvents was studied by Armes et al.[23] They succeeded to polymerize METAC in water but the product had rather high polydispersity. Controlled polymerization of METAC in methanol and methanol/water solutions was accompanied by transesterification of the monomer producing MMA. Transesterification of METAC was avoided by using 2-propanol instead of methanol, and poly-METAC with relatively low polydispersity was synthesized. To our knowledge, there is no publication describing AGET or SARA ATRP of METAC.

In this paper, we report polymerization of METAC and synthesis of well-defined cationic polymers by CRP using the methods of AGET ATRP and SARA ATRP. Nevertheless AGET system with automatic injection of the reducing agent ascorbic acid demonstrated controllable polymerization with no signs of transesterification, polymerization under especially developed conditions of SARA ATRP in aqueous solutions was even more promising, enabling one to get cationic polymers with low polydispersity up to high conversions. A modification of SARA system for aqueous solutions is proposed, which is based on the use of supplemental redox intermediates mediating electron transfer between zerovalent metal and the deactivator Cu^{II}/L and ensuring steady generation of the activator *in situ*.

EXPERIMENTAL SECTION

Materials. [2-(Methacryloyloxy)ethyl]trimethylammonium chloride (METAC, 75% aqueous solution, Aldrich) was purified by passing the monomer through a column filled with basic alumina (Type 5016A, Fluka). Copper(II) chloride ($CuCl_2$, ≥97%, Aldrich), copper(I) chloride (CuCl, 99.999%, Aldrich), ethyl bromoisobutyrate (EBiB, 98%, Aldrich), ascorbic acid (AscA, 99%, Aldrich), iron(III) chloride hexahydrate ($FeCl_3 \times 6H_2O$, 99%, Aldrich), hydroquinone (HQ, 99%, Aldrich) were used as received. Oxidized forms of ascorbic acid and hydroquinone were prepared by magnetic stirring 0.03 M solutions of these substances in methanol overnight in air. Efficiency of oxidation of AscA and HQ was confirmed by cyclic voltammetry. Tris[2-(dimethylamino)ethyl] amine (Me_6TREN) and tris[(2-pyridyl)-methyl] amine (TPMA) were prepared by the methods described elsewhere.[24,25]

AGET ATRP of METAC. A 10 ml aliquot of methanol, 5.33 g of METAC 75% aqueous solution (4.00 g, 1.93×10^{-2} mol), 25.9 mg of $CuCl_2$ (1.93×10^{-4} mol), 44.4 mg of Me_6TREN (1.93×10^{-4} mol), and 37.6 mg of EBiB (1.93×10^{-4} mol) were placed into a round-bottom flask equipped with a Teflon-coated stir bar. After sealing with a rubber septum, the flask was deoxygenated for 30 min by purging Argon (Ar). To start polymerization, 1 mL of deoxygenated 0.03 M AscA methanol solution (5.1 mg, 2.89×10^{-5} mol) was injected during 4 min to the above solution using Ar-purged chromatographic pump P-500. Polymerization was carried out at room temperature for 18 h. The polymer was precipitated by pouring the reaction mixture to 10-fold excess of acetone. Dissolution in methanol and precipitation to acetone were repeated three times until white powder of poly-METAC was obtained. The product was dried in a vacuum oven at 40 °C until constant weight. Yield: 2.7 g (67.5%).

SARA ATRP of METAC. Components of the reaction mixture and their amounts were the same as in AGET procedure described above but the oxidized form of AscA (5.1 mg, 2.89×10^{-5} mol) was used. After sealing with a rubber septum, the flask was deoxygenated for 30 min by purging Ar, and then 0.5 g of metallic copper beads were added to the flask. Polymerization was carried out at room temperature for 18 h. All insoluble components of the reaction mixture were removed by filtration. Purification of the product was the same as in AGET procedure. Yield: 3.9 g (97%).

Size Exclusion Chromatography. Polymer characterization by size exclusion chromatography (SEC) was carried out on a Viscotek TDAmax system equipped with a triple-detection array (TDA305) consisting of refractive index detector, right-angle (90°) and low-angle (7°) light scattering detectors, and four-capillary bridge viscosity detector. A column was from Viscotek, A6000M, 300 × 8.0 mm, General Mixed for aqueous solutions. 0.3 M aqueous $NaNO_3$ solution was used as a mobile phase at a flow rate of 0.5 mL/min. The whole system, including columns and detectors, was maintained at 35 °C. The injection-loop volume was 100 μL, concentration of polymer 2.0 to 10.0 mg/mL. OmniSEC software from Viscotek was used to collect and analyze the data.

RESULTS AND DISCUSSION

Polymerization of METAC by AGET ATRP. In order to evaluate advantages and drawbacks of SARA ATRP of the cationic monomer METAC in aqueous and water-containing solutions, normal, AGET, and SARA ATRP of this monomer were carried out in parallel.

Normal ATRP of METAC was not successful irrespective of the solvent used. During polymerization in aqueous solution, monomer conversion was less than 10%, and the product had high polydispersity (M_w/M_n about 2). In methanol solution, transesterification of METAC was much faster than polymerization giving no polymer. In water/2-propanol (1:3) mixture, polymerization proceeded under heterogeneous conditions giving moderate yield (about 30%) and again was badly controlled ($M_w/M_n > 2$). These results are consistent with the data published before by Armes et al.[23] Detailed description of normal ATRP of METAC is presented in the Supporting Information.

In AGET ATRP, the activator Cu^I/L usually is generated by reduction of oxidatively stable Cu^{II}/L using reducing agents ascorbic acid[4] or tin ethylhexanoate.[3] Tin ethylhexanoate is not suitable for aqueous solutions because of fast hydrolysis of this compound. The most popular reducing agent in AGET ATRP is ascorbic acid (AscA). It was determined[4] that the ratio of the activator Cu^I/L to the deactivator Cu^{II}/L and, consequently, the molecular weight distribution of the polymer was dependent on concentration of AscA in the reaction mixture.

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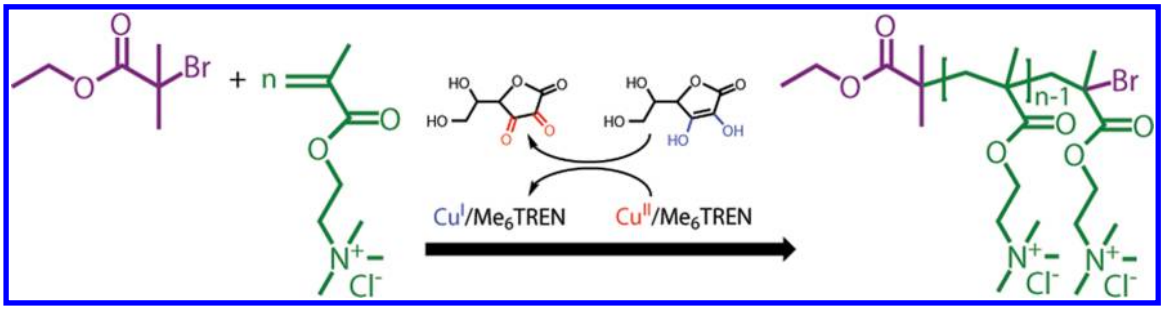
Scheme 1. AGET ATRP of METAC Using Ascorbic Acid as a Reducing Agent



Polymerization of METAC was conducted in methanol/water mixture (75/25, wt/wt) varying concentration of both Cu^{II}/Me$_6$TREN complex and AscA (Scheme 1). It was observed that AscA was lowering pH of methanol/water solutions thus eliminating transesterification reactions and making such solutions suitable for polymerization of METAC. Polymerization of METAC at low concentrations of Cu^{II}/L was badly controlled (Table 1, entries 1 and 2). This could be explained by side reactions like oxidation and disproportionation of the activator which have larger impact at low concentrations of Cu^{II}/L. Higher concentrations of Cu^{II}/L (Table 1, entries 3−5) enabled to achieve better control over polymerization processes producing poly-METAC with low polydispersity.

Table 1. Results of METAC Polymerization by AGET ATRP

no.	[METAC]/[EBiB]/[CuCl$_2$]/[Me$_6$TREN]	AscA, mol % to [Cu^{II}]	convn,[a] %	$M_n \times 10^{-3}$, theor	$M_n \times 10^{-3}$, SEC	M_w/M_n
1	100/1/0.1/0.1	15	7.2	2.5	21.4	1.55
2	100/1/0.5/0.5	15	36.3	11.5	24.8	1.41
3	100/1/1/1	15	67.5	21.2	23.5	1.25
4	100/1/1/1	10	55.2	17.3	18.7	1.26
5	100/1/1/1	5	25.7	8.2	14.2	1.28
6	100/1/1/1	30	85.0	26.2	26.7	1.31
7	100/1/1/1	60	97.5	31.1	30.6	1.38

[a]Conversion of the monomer after 18 h of polymerization.

It was determined that reproducibility of the results of AGET ATRP of METAC was bad, i.e., parameters of poly-METAC (molecular weight, polydispersity) synthesized under the same conditions and the same ratio of the components were varying. Analysis of this phenomenon brought to idea that bad reproducibility of the results is related to concentration fluctuations of AscA in the reaction mixture. Controllable dosing of methanolic AscA solutions was realized by adjusting an argon-purged chromatographic pump with varying pumping speed rates.

Using a chromatographic pump, AscA solution was injected into the polymerization mixture at constant rate, and the injection rate was varied searching for the optimal time of AscA dosing. Figure 1 represents the dependences of METAC conversion and M_w/M_n of poly-METAC on dosing time of the reducing agent. It is evident that the highest conversion of METAC and the lowest polydispersity of poly-METAC are achieved at a certain injection time which in the case of dosing of 1 mL 0.03 M solution of AscA corresponds to 4 min. Optimal dosing time (or, the same, optimal dosing rate) is likely related to equilibrium of the redox reaction which at

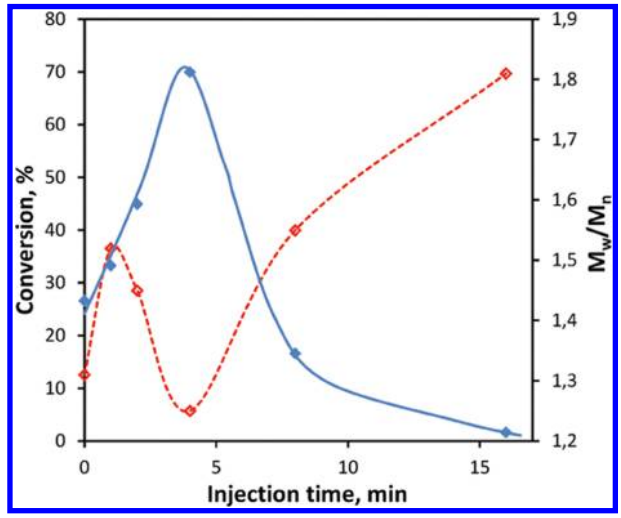


Figure 1. Conversion of the monomer after 18 h of polymerization (filled dots) and polydispersity index M_w/M_n of the polymer (blank dots) vs injection time of 1 mL of 0.03 M AscA solution under AGET ATRP of METAC.

appropriate dosing rate produces the optimal ratio of the activator Cu^{I}/L to the deactivator Cu^{II}/L.

The effect of concentrations of the reducing agent AscA and the deactivator Cu^{II}/L on the parameters of poly-METAC was studied at the optimal injection rate 0.25 mL/min (Table 1). Low concentration of Cu^{II}/L in respect to the initiator EBiB was noneffective giving low conversion of the monomer and relatively large polydispersity of the polymer. It was determined that the optimal conditions for AGET ATRP of METAC were at the equimolar ratio of EBiB and Cu^{II}/L. Polymerization was well controllable even at low concentration of AscA but higher concentrations of AscA helped to reach higher conversions of the monomer (Table 1, entries 6 and 7). The optimal concentration of AscA in respect to Cu^{II} was 15 mol % enabling to reach nearly 70 mol % conversion of the monomer. Using higher AscA concentrations, conversion of the monomer was over 90 mol % but polydispersity of the polymer was higher in those cases (Figure 2). At low conversions of the monomer, molecular weight of poly-METAC was higher than theoretically calculated but polydispersity was low (Figure 2). Larger polydispersity of poly-METAC synthesized at conversions of the monomer over 80% can be related to increased viscosity of the reaction mixture which favors coupling reactions.

Thus, AGET ATRP of METAC with controllable dosing of ascorbic acid allowed good control over molecular weight and molecular weight distribution of the polymer. The only inconveniences were related with the dosing of the reducing agent and necessity to stop polymerization at moderate

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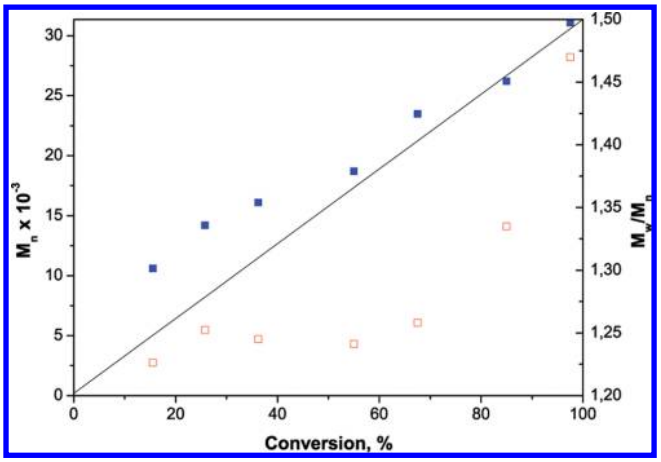

Figure 2. Dependence of molecular weight (filled dots) and polydispersity index (blank dots) of poly-METAC on conversion of the monomer under AGET ATRP conditions: The straight line represents evolution of theoretically calculated molecular weight.

conversions since at high conversions the control over polymerization was partially lost.

Polymerization of METAC by SARA ATRP in Methanol/Water Solutions. For SARA ATRP of METAC, four reducing agents most commonly used in other studies were tested and compared: aluminum (Al), zinc (Zn), iron (Fe), and copper (Cu). The components of the reaction mixture were as follows: monomer METAC, initiator EBiB, deactivator Cu^{II}/L, and supplemental activator and reducing agent zerovalent metal. It was determined that aluminum and zinc were inappropriate because of amphoteric properties and possibility to form hydroxides in aqueous solutions. Indeed, reaction mixtures containing aluminum or zinc after 18 h of SARA ATRP became alkaline (pH 9−10), and white solids precipitated. No polymer was detected in the reaction products. Moreover, transesterification of METAC can take place in alkaline solutions of these reducing agents (see Supporting Information). The reaction mixture containing zerovalent copper remained without changes during 18 h but did not give the polymer as well. At the initial ratio of the components of the reaction mixture [METAC]/[EBiB]/[$CuCl_2$]/[Me_6TREN] = 200/1/1/1, the only presence of zerovalent iron was favorable for polymerization (Table 2, entry 1). Conversion of the monomer was very high, and molecular weight of poly-METAC was close to theoretically calculated with moderate polydispersity (M_w/M_n = 1.48) showing a certain effect of side reactions.

Table 2. Results of Polymerization of METAC by SARA ATRP. [METAC]/[EBiB]/[$CuCl_2$]/[Me_6TREN] = 200/1/1/1 (mol/mol)

no.	SRI	Me^0	convn,[a] %	$M_n \times 10^{-3}$, theor	$M_n \times 10^{-3}$, SEC	M_w/M_n
1	−	Fe	95	39.6	42.3	1.48
2	AscA	Al	96	40.0	37.0	1.51
3	AscA	Zn	98	40.9	40.6	1.41
4	AscA	Fe	67	28.0	27.3	1.27
5	AscA	Cu	62	25.9	26.5	1.28
6	$FeCl_3$	Cu	58	24.2	24.9	1.25
7	HQ	Cu	60	25.1	25.4	1.34
8	$FeCl_3$	Fe	87	36.3	37.0	1.29

[a]Conversion of the monomer after 18 h of polymerization.

The reaction mixture containing iron was clear but of lightly brown color, like iron(III) chloride aqueous solutions. We suppose that in aqueous solutions containing zerovalent iron, ions of iron(II) are formed. Fe^{II} takes part in redox reaction with the deactivator Cu^{II}/L which generates the activator Cu^{I}/L favoring ATRP processes. In the solutions containing zerovalent copper, Cu^{I} ions are formed instead of Fe^{II}. It is known that Cu (I) chloride is not stable in aqueous solutions and susceptible to disproportionation.[24,26]

Copper and iron are good supplemental activators and reducing agents for SARA ATRP of MA in nonpolar solvents (DMSO, acetonitrile).[8] At the surface of zerovalent metals, redox reaction between reducing metal Me^0 and oxidizing deactivator Cu^{II}/L takes place. As a result of this reaction, activator Cu^{I}/L and the ions of a reducing metal are generated. The activator Cu^{I}/L diffuses away from the surface of the metal and triggers polymerization. In organic solutions, where disproportionation of the activator Cu^{I}/L is marginal, this scheme works fine. In aqueous solutions, however, this scheme fails, as it was shown by our experiments studying polymerization of METAC in the presence of Cu^0. Likely, disproportionation of the activator starts at the surface of the reducing metal, and this process is fast competing with the diffusion of the activator.

In order to lower or bypass disproportionation of Cu^{I}/L, an idea of supplemental redox intermediates (SRI) for SARA ATRP in aqueous solutions was developed and tested. The role of these intermediates is mediation in transfer of electrons from zerovalent metals to Cu^{II}/L and generation of the activators Cu^{I}/L *in situ*. The main requirement for SRI is good stability in aqueous solutions in both forms, oxidized and reduced. Another requirement is related to elimination of parallel redox reactions with participation of the intermediate which can generate the activator by another mechanism (e.g., AGET). Usually, control of ATRP is reduced if polymerization is triggered by two competing mechanisms ensuring different rates of generation of the activator.

To check this presumption, a solution of ascorbic acid (AscA) oxidized in air overnight was injected into methanol/water solution of METAC containing necessary components of ATRP system. No polymerization took place during several hours. When beads of aluminum, zinc, iron or copper were added to the reaction mixtures containing oxidized AscA, polymerizations started in all the cases (Table 2, entries 2−5). SARA ATRP of METAC in the presence of aluminum or zinc was badly controlled which likely was related to high activity of these reducing agents, similarly as it was shown before by Matyjaszewski et al.[8] Iron or copper, present together with the oxidized AscA (Table 2, entries 4 and 5), favored good control over molecular weight and formation of poly-METAC with low polydispersity. Instead of ascorbic acid, other SRI like iron(III) chloride or oxidized hydroquinone were tested for SARA ATRP of METAC in aqueous solutions together with reducing metals iron or copper (Table 2, entries 6−8). All SRI were efficient giving good control over polymerization. Interestingly, the presence of hydroquinone which is used usually as inhibitor for radical processes, did not stop polymerization since it acted as a component of the SARA system.

A series of poly-METAC was prepared by varying concentration of Cu^{II}/L, AscA, or iron(III) chloride as SRI and iron or copper as reducing metals (Table 3). In most cases,

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Table 3. Results of Polymerization of METAC by SARA ATRP

no.	[METAC]/[EBiB]/ /[$CuCl_2$]/[Me_6TREN]	SRI	Me^0	convn,[a] %	$M_n \times 10^{-3}$, theor.	$M_n \times 10^{-3}$, SEC	M_w/M_n
1	200/1/1/1	$FeCl_3$	Cu	86	35.9	35.0	1.28
2	200/1/0.5/0.5	$FeCl_3$	Cu	80	33.4	35.8	1.25
3	200/1/0.1/0.1	$FeCl_3$	Cu	70	29.3	26.5	1.33
4	200/1/0/1	$FeCl_3$	Cu	0	–	–	–
5	200/1/1/1	AscA	Cu	85	35.5	35.0	1.29
6	200/1/0.5/0.5	AscA	Cu	73	30.5	30.1	1.25
7	200/1/0.1/0.1	AscA	Cu	92	38.4	38.0	1.33
8	200/1/0/1	AscA	Cu	0	–	–	–
9	200/1/1/1	$FeCl_3$	Fe	90	37.6	37.0	1.30
10	200/1/0.5/0.5	$FeCl_3$	Fe	73	30.5	28.8	1.27
11	200/1/0.1/0.1	$FeCl_3$	Fe	77	32.2	31.0	1.31
12	200/1/0/1	$FeCl_3$	Fe	56	23.4	36.2	2.27
13	200/1/1/1	AscA	Fe	83	34.7	35.2	1.27
14	200/1/0.5/0.5	AscA	Fe	78	32.6	32.1	1.26
15	200/1/0.1/0.1	AscA	Fe	80	33.4	32.8	1.40
16	200/1/0/1	AscA	Fe	48	20.1	33.0	2.52

[a]Conversion of the monomer after 18 h of polymerization.

control of polymerization was very good enabling to synthesize poly-METAC with predetermined molecular weight and rather low polydispersity. The worse results were at low Cu^{II}/L concentrations or in the samples were no $CuCl_2$ was added. Without doubt, aqueous SARA ATRP of METAC in the presence of SRI was better controllable than AGET ATRP of the same monomer, especially at high conversions (Figure 3). Other advantages of SARA ATRP in the presence of SRI compared to AGET ATRP are related to simpler technical implementation and better reproducibility of the results.

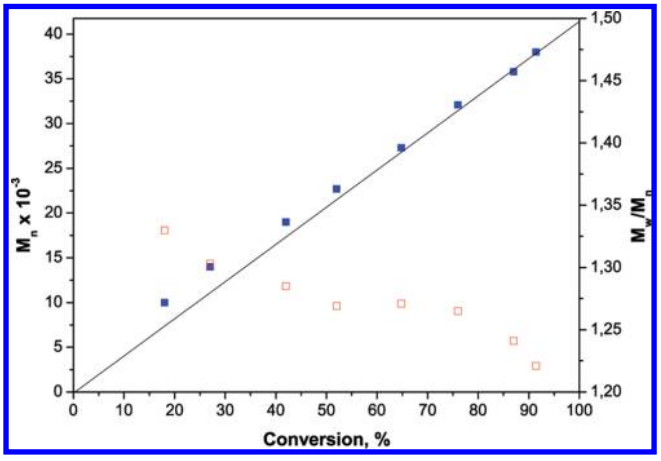

Figure 3. Dependence of molecular weight (filled dots) and polydispersity index (blank dots) of poly-METAC on conversion under SARA ATRP conditions in methanol/water solution. The straight line represents evolution of theoretically calculated molecular weight.

One should notice, however, that PDI of poly-METAC, synthesized by both techniques, AGET ATRP and SARA ATRP in the presence of SRI, is not very low, usually about 1.25−1.30. Increased polydispersity of poly-METAC could be related to several features of polymerization of a salt (Cl^- anion containing) monomer in aqueous solutions like high ionic strength of the reaction mixture, halogen exchange between Cl^- ions (from METAC and $CuCl_2$) and Br^- ions (from EBiB), and competitive binding between Cl^- and Cu. Besides, according to recent data,[27] halogen exchange is preferable since it supports better control over polymerization. Unfortunately, because of very high concentration of Cl^- ions in METAC solution compared to the concentration of Br^- ions, halogen exchange leads to Cl-terminated growing chains (no further halogen exchange).

To check livingness of poly-METAC synthesized under conditions of SARA ATRP in the presence of SRI, chain extension reactions were performed under the same conditions. For the chain extension, poly-METAC was used as a macroinitiator, and METAC, 1-vinyl-2-pyrrolidinone (VP) and 4-vinylpyridine (VPy) were polymerized resulting in poly-METAC with higher molecular weight or block copolymers poly-METAC-*block*-poly-VP and poly-METAC-*block*-poly-VPy. Chain extension was perfectly controlled giving polymers and block copolymers with PDI 1.13−1.16, even lower than that of primary poly-METAC. Thus, poly-METAC prepared by SARA ATRP in the presence of SRI is efficient macroinitiator for chain extension polymerization of various monomers and is suitable for the synthesis of diblock copolymers. Detailed description of chain extension reactions is presented in the Supporting Information.

Mechanism of SARA ATRP in Aqueous Solutions in the Presence of SRI. In order to ascertain the role of supplemental redox intermediate (SRI) participating in competitive redox reactions occurring under conditions of SARA ATRP in aqueous solutions, cyclic voltammetry (CV) measurements of methanol/water solutions of METAC containing various electrochemically active components of ATRP system were done. Detailed descriptions of CV curves as well as quantitative data summarizing oxidation and reduction potentials of the species taking part in redox reactions are presented in the Supporting Information.

A model of electron transfer in aqueous SARA ATRP systems containing SRI was build using oxidation and reduction potentials measured by CV (Figure 4). This model displays oxidation and reduction potentials of typical constituents of aqueous SARA ATRP in regard to the oxidation potential of the deactivator Cu^{II}/L (dashed line). For simplicity and evidence, oxidized forms of species are shown on oxidation potentials, and reduced forms of the same species on reduction potentials (Figure 4). According to the model, SRI suitable for SARA

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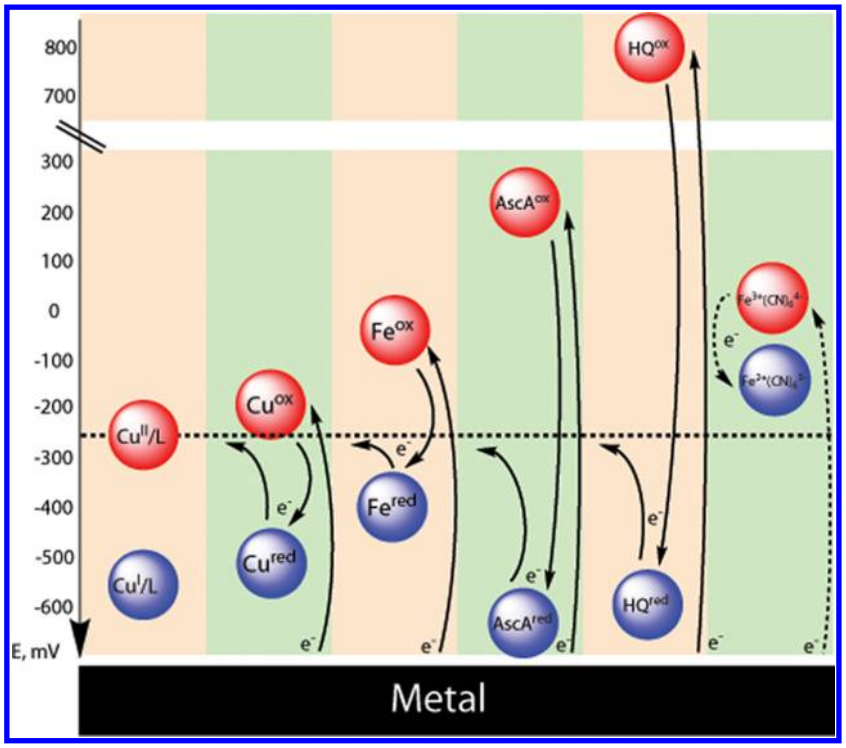

Figure 4. Reduction (blue) and oxidation (red) potentials of various components present in methanol/water solutions of METAC under conditions of SARA ATRP. Plain arrows show possible way of electron transfer from a zerovalent metal through SRI to the deactivator Cu^{II}/L. Dashed arrows represent the way of electron transfer which ends before reaching the deactivator Cu^{II}/L.

ATRP should have reduction potential lower than the oxidation potential of the deactivator Cu^{II}/L. In turn, oxidation potential of SRI should be higher compared to the oxidation potential of the deactivator Cu^{II}/L, otherwise an electron from a zerovalent metal will be transferred directly to the deactivator Cu^{II}/L, like in SARA ATRP without SRI. Oxidation potential of SRI much higher than that of Cu^{II}/L is preferable since the driving force of the redox reaction between zerovalent metal and oxidized SRI is higher in that case, enabling a higher rate of the redox reaction. If the above requirements are fulfilled, an electron from a zerovalent metal is transferred through SRI to the deactivator Cu^{II}/L, which generates Cu^{I}/L (Figure 4). Oxidized ascorbic acid, oxidized hydroquinone, and iron(III) chloride are proper SRI, fulfilling the above requirements. It was determined that $K_3[Fe(CN)_6]$ was not suitable as SRI because of reduction potential higher than oxidation potential of Cu^{II}/L (Figure 4).

The role of SRI in aqueous SARA ATRP is demonstrated by the reactions presented in Scheme 2. SRI in its oxidized form takes part in redox reaction with zerovalent metal. Reduced form of SRI produced this way reacts with the deactivator Cu^{II}/L generating activator Cu^{I}/L; during the last reaction, the oxidized form of SRI is restored. As it is shown by the sum reaction, SRI is not used in this redox process, it just mediates in electron transfer from Me^0 to Cu^{II}/L. Nevertheless, SRI is an essential component of the system, maintaining a proper ratio of the activator Cu^{I}/L to the deactivator Cu^{II}/L.

Scheme 2. Intermediate (1, 2) and Sum (3) Redox Reactions Occurring in SARA ATRP System Containing SRI, Where Me^{ox} Represents a Metal with the Lowest Oxidation Degree, Not Necessarily 1

$$Me^0 + SRI^{ox} \rightleftharpoons Me^{ox} + SRI^{red} \quad (1)$$

$$SRI^{red} + Cu^{II}/L \rightleftharpoons Cu^{I}/L + SRI^{ox} \quad (2)$$

$$Me^0 + Cu^{II}/L \rightleftharpoons Me^{ox} + Cu^{I}/L \quad (3)$$

One should notice that the only reactions presented in Scheme 2 are permissible by redox potentials of the components of the reaction mixture and lead to the steady generation of the activator Cu^{I}/L. Direct redox reaction between Me^0 and Cu^{II}/L shown by the sum equation in Scheme 2 is possible but proceeds with much lower rate compared to the rate of the two reactions involving SRI because of lower driving force. Redox reaction between AscA and Cu^{II}/L taking part in AGET/ARGET systems[4] cannot be realized in this case since initial SRI is in its oxidized form.

Scheme 2 shows that during successive redox reactions occurring in the presence of SRI, zerovalent metal gradually dissolves, converting to the ion with the lowest degree of oxidation. If zerovalent metal is copper, Cu^{I} formed is unstable in aqueous solutions and tends to disproportionate producing Cu^0 and Cu^{II}. This leads to an increase in concentration of Cu^{II} in the system but not in concentration of Cu^{I} since the last is controlled by a fixed concentration of SRI. If zerovalent metal is iron, Fe^{II} is produced which virtually can compete with Cu^{I} for the same ligands L and take part in activation of ATRP process; the use of Fe^{II}/L instead of Cu^{I}/L is known and efficient in some cases.[28] This scheme would be undesirable because of two competitive equilibriums Cu^{I}/Cu^{II} and Fe^{II}/Fe^{III} controlling polymerization which could lead to increased polydispersity of the polymers. Fortunately, this is not the case. CV curves of ATRP systems containing SRI and zerovalent iron (see Supporting Information) were characterized by potentials characteristic for the electron transfer $Cu^{II} \leftrightarrow Cu^{I}$ only, with

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no signs of the redox reaction Fe^{II}/Fe^{III}. Thus, zerovalent iron can be used as supplemental activator and reducing agent alongside with SRI for aqueous SARA ATRP.

General scheme of SARA ATRP of hydrophilic monomers in aqueous solutions containing SRI is presented in Scheme 3.

Scheme 3. General Scheme of SARA ATRP in Aqueous Solutions Containing SRI

Thus, our studies revealed that there are essential differences between SARA ATRP systems in organic and aqueous solutions. In order to ensure steady generation of the activator Cu^I/L, a supplemental redox intermediate together with zerovalent metal as a supplemental activator and reducing agent should be used in aqueous solutions.

Versatility of the SARA ATRP system containing SRI for polymerization of hydrophilic monomers in aqueous solutions needs to be examined studying polymerization of other monomers, testing more SRI and combining them with various ligands. Our recent data revealed that the choice of a ligand is crucial. When TPMA was used instead of Me_6TREN under SARA ATRP of METAC in the presence of SRI, the polymers synthesized were more polydisperse and with bimodal MWD (see Supporting Information). Possibly, the rate of generation of the activator Cu^I/L according to the proposed mechanism depends on the ligand. When Me_6TREN is used as a ligand, the proposed mechanism distinctly prevails but the situation is more complex in the case of TPMA. More detailed study is required to compare rates of generation of the activator Cu^I/L by both mechanisms, SARA and SARA in the presence of SRI, to ascertain possibilities using other ligands than Me_6TREN for SARA ATRP of hydrophilic monomers.

CONCLUSIONS

AGET ATRP with controllable dosing of ascorbic acid led to good control over molecular weight and molecular weight distribution under polymerization of the cationic monomer 2-[(methacryloyloxy)ethyl]trimethylammonium chloride (METAC) in methanol/water solutions. The use of supplemental redox intermediates (SRI) for SARA ATRP in organic/water solutions was proposed and demonstrated enabling to get even better results as by AGET ATRP. It was shown by cyclic voltammetry measurements that only SRI with the oxidation potentials higher and reduction potentials lower than the oxidation potential of the deactivator Cu^{II}/L were suitable. Ascorbic acid and hydroquinone in their oxidized form, and iron(III) chloride are between preferable SRI but not limit the scope. A mechanism of generation of the activator Cu^I/L in the presence of zerovalent metals and SRI in aqueous solutions of SARA ATRP was proposed, and the process was named ISARA—intermediate for supplemental activator and reducing agent.

ISARA has several advantages compared to AGET ATRP, the main being simpler technical implementation, lower sensitivity to oxygen, better reproducibility of the results, and good control over polymerization up to high conversions of the monomers. This method opens new possibilities for ATRP in aqueous and water-containing solutions, and is especially suitable for polymerization of hydrophilic and water-soluble monomers.

ASSOCIATED CONTENT

Supporting Information

Experimental details, including characterization, polymerization of METAC by normal ATRP, polymerization of METAC by SARA ATRP using TPMA as a ligand, and chain extension of poly-METAC by chains of METAC and other vinyl monomers and cyclic voltammetry data of aqueous solutions of METAC containing various components of ISARA ATRP. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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