

Atom Transfer Radical Polymerization of Methacrylic Acid: A Won Challenge

Marco Fantin,^{§,†} Abdirisak A. Isse,^{*,§} Alfonso Venzo,[‡] Armando Gennaro,^{*,§} and Krzysztof Matyjaszewski^{*,†}

[§]Department of Chemical Sciences, University of Padova, Via Marzolo 1, 35131 Padova, Italy

[‡]ENI–CNR, Department of Chemical Sciences, University of Padova, Via Marzolo 1, 35131 Padova, Italy

[†]Center for Molecular Engineering, Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213, United States

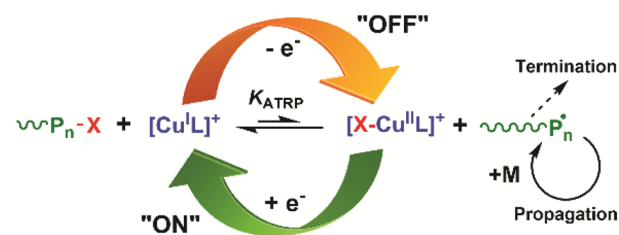
S Supporting Information

ABSTRACT: Polymerization of acidic monomers is one of the biggest challenges for atom transfer radical polymerization (ATRP). An intramolecular cyclization reaction leading to the loss of the C–X chain-end functionality was found to be the main reason for the partial termination of the growing polymer chains. Three approaches were used to overcome this problem: using Cl as the chain-end halogen, lowering the pH (to 0.9), and increasing polymerization rate. Methacrylic acid (MAA) was polymerized by both electrochemically mediated ATRP and supplemental activator and reducing agent ATRP up to high conversion (>90%), in $t \leq 4$ h at 25 °C, using inexpensive and nontoxic reagents (NaCl, diluted HCl, water). Control over molecular weight (MW) dispersity was satisfactory, and MWs were in agreement with theoretical values. The “livingness” of the process was confirmed by an electrochemical switch, used to repeatedly and periodically deactivate/reactivate growing chains.

Atom transfer radical polymerization (ATRP) is a powerful controlled radical polymerization technique,¹ used to prepare polymers with well-defined architectures, predetermined molecular weights (MW), and low dispersities ($D < 1.5$).² Usually, ATRP is catalyzed by a copper–amine ligand complex through a reversible equilibrium involving the activator and deactivator complexes, $[\text{Cu}^{\text{I}}\text{L}]^+$ and $[\text{X-Cu}^{\text{II}}\text{L}]^+$ ($\text{X} = \text{Cl}, \text{Br}$), respectively. $K_{\text{ATRP}} \ll 1$ guarantees that the vast majority of the propagating chains is in the dormant state ($\text{P}_n\text{-X}$), while the concentration of active radicals (P_n^\bullet) is low to minimize the occurrence of radical termination reactions and promote concurrent growth of all polymer chains. In electrochemically mediated ATRP (eATRP, Scheme 1), the Cu^{I} activator complex is (re)generated by reduction of Cu^{II} at a working electrode. In supplemental activator and reducing agent (SARA) ATRP, Cu^{I} is regenerated by comproportionation between Cu^0 and Cu^{II} . These techniques use very low catalyst loadings.³

One of ATRP's advantages is a large range of polymerizable monomers, except those without radical-stabilizing substituents or acidic monomers, for which ATRP has shown some limitations. For acidic monomers, reasons hypothesized for

Scheme 1. Low-ppm ATRP with (Re)generation of the Active Catalyst by Electrochemical Reduction



the lack of success include ligand protonation at low pH,^{4,5} competitive coordination of the carboxylate moieties to copper,⁴ and displacement of the halide anion from the Cu^{II} deactivator complex;⁵ however, no definitive answer was provided. Controlled ATRP of (co)polymers containing carboxylic acid groups, such as methacrylic acid (MAA), can pave the way to the development of new materials with unique complexing ability, pH responsiveness, and biocompatibility.

Although both RAFT⁶ and NMP⁷ can be used for the direct polymerization of MAA and acrylic acid, the synthesis of controlled acidic polymers is still a challenge for ATRP. Until now, ATRP allowed the synthesis of only well-controlled ($D < 1.5$) random copolymers with a low ($\leq 20\%$) MAA content.⁸ For the synthesis of well-defined acidic homopolymers, ATRP of protected monomers was employed, requiring polymerization in organic solvents, followed by deprotection and purification.⁹ ATRP of sodium methacrylate was reported¹⁰ but required high concentration of $\text{CuBr}/\text{bipyridine}$ ($>10\,000$ ppm, molar ratio of Cu catalyst to monomer), high temperature (90 °C), and long reaction times (up to 21 h).

Direct polymerization of MAA in its acidic (non-ionized) form has several advantages: (i) k_p of MAA is 10 times higher than that of sodium methacrylate;¹¹ (ii) polymerization should not be inhibited by the buildup of polyanionic charge on the polymer backbone;¹⁰ (iii) carboxylic acids are much weaker nucleophiles and complexing agents than carboxylate anions (they can be more easily purified and may not compete for Cu ions with ATRP amine ligands or halide ions); and (iv) titration/neutralization of the monomer is not required.

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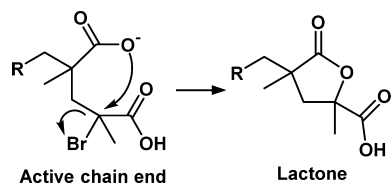
Developing a well-controlled ATRP of MAA requires understanding the reasons leading to the difficulties in controlling, or even carrying out, the polymerization. Thus, the ATRP system composed of the catalyst $\text{Cu}^{\text{II}}\text{X}_2/\text{TPMA}$ and the initiator 2-hydroxyethyl α -bromoisobutyrate (HEBiB) was investigated in aqueous MAA. Tris(2-pyridylmethyl)amine (TPMA) was selected because it forms a highly stable Cu^{I} complex,¹² suppresses disproportionation,^{5,13} is less basic than alkylamine ligands, and was already used for ATRP under acidic conditions.⁵

Cyclic voltammetry (CV) of $[\text{Cu}^{\text{II}}\text{TPMA}]^+$ in the polymerization mixture (10% v/v MAA in water + 0.1 M NaBr, Figure S1) indicated that the Cu complex has a suitable catalytic activity. Moreover, the initiator was not hydrolyzed in the presence of MAA (see Supporting Information (SI)). Last, the Cu–X bond of the deactivator complex $[\text{X-Cu}^{\text{II}}\text{TPMA}]^+$ is sufficiently stable in the presence of MAA: a halidophilicity constant $K_{\text{Cl}} = 38 \text{ M}^{-1}$ was determined by vis–NIR titration for $[\text{Cu}^{\text{II}}\text{TPMA}]^+$ in 20% MAA in water (Figure S2).

By recording the total consumed charge (Q) during an $e\text{ATRP}$ experiment, it was determined that $\leq 9\%$ of chains terminated by radical–radical reactions (see SI). Such a value is compatible with a controlled radical polymerization.¹⁴ Therefore, most of the chain-end functionality was not lost through radical termination, but rather through a different pathway.

PMAA with a low degree of polymerization (DP) was prepared by SARA ATRP to more precisely analyze the retained (or lost) chain ends via NMR (conditions: $C_{\text{M}}:C_{\text{RX}}:C_{\text{Cu}(\text{OTf})_2}:C_{\text{TPMA}}:C_{\text{NaBr}} = 10:1:0.001:0.03:5$, in 5% v/v MAA in D_2O , pH 2.2, $V_{\text{tot}} = 5 \text{ mL}$, 10 cm Cu wire with 1 mm diameter, $\text{RX} = \alpha$ -bromoisobutyric acid, BiBA). The reaction stopped after 1 h, suggesting the loss of active C–Br chain-end functionality. 1D and 2D NMR spectra of the polymerization mixture (Figures S4–S8) showed the presence of a lactone, plausibly formed via intramolecular substitution at the chain end (Scheme 2). The cyclization continued throughout the

Scheme 2. PMAA Chain-End Cyclization



polymerization (Figure S9), favored by the presence of Cu^{I} . FT-IR of the obtained PMAA further confirmed the formation of a lactone (Figure S10): a peak shoulder at $\nu = 1770 \text{ cm}^{-1}$ was attributed to the stretching of a lactone carbonyl.

Once the main cause of termination was identified, three strategies to diminish cyclization were applied, directed toward the leaving group (chain-end Br was replaced by Cl) and the

nucleophile (pH was lowered to reduce the concentration of carboxylate anions). Finally, ATRP was accelerated, in order to reduce the contribution of the cyclization. The approach reported here is a shift of paradigm, as it is based on strongly acidic rather than neutral/basic conditions.

Polymerization of MAA was first studied by $e\text{ATRP}$, which employs an external stimulus (applied potential, E_{app}) and is only marginally influenced by modifications of the polymerization media. Polymerizations were performed with appropriate concentrations (0.1–0.3 M) of X^- to prevent the dissociation of the ternary deactivator complex $[\text{X-Cu}^{\text{II}}\text{L}]^+$ (e.g., only 21% dissociated to $\text{Cl}^- + [\text{Cu}^{\text{II}}\text{L}]^{2+}$ at 0.1 M NaCl).

Switching from 0.1 M NaBr to 0.1 M NaCl as supporting electrolyte resulted in a remarkable improvement in the $e\text{ATRP}$ of MAA: conversion increased from 7% to 43% (Table 1), while lifetime of growing chains increased from 1 to 3 h. ^1H NMR showed that the chain-end cyclization was significantly hampered when NaCl was used instead of NaBr (Figure S9); Cl^- anion is a poorer leaving group than Br^- and is displaced less readily from the chain ends. When a high concentration of Cl^- was used in the presence of HEBiB as initiator, a halogen exchange reaction occurred at the early stage of the process,¹⁵ converting most chain ends to C–Cl. The highly active RBr initiator (more active than $\text{P}_n\text{-Cl}$) assured fast initiation and concurrent growth of all chains.

pH dramatically affects the redox properties of the catalyst (Figure S11). Changing pH from 2.2 to 0.9 makes E° of the complex in 10% v/v MAA in water shift from -0.20 to -0.06 V vs SCE. This E° shift can be used to estimate a decrease in K_{ATRP} of 2–3 orders of magnitude.¹⁶ Therefore, the activity of the complex at pH 0.9 should be similar to that in polar organic solvents (e.g., DMSO or DMF, where K_{ATRP} is 2 and 3 orders of magnitude smaller than that in water, respectively^{16b,17}). Figure S11b further confirmed the predicted large decrease of $[\text{Cu}^{\text{II}}\text{TPMA}]^{2+}$ catalytic activity with decreasing pH: in the presence of α -bromophenylacetic acid as initiator, the cathodic current drastically dropped when MAA, or MAA + HCl, was added to water. Nevertheless, at pH 0.9, a cathodic current (I_{pc}) of $35 \mu\text{A}$ was recorded. This value is more than 3 times greater than I_{pc} of the catalyst alone, clearly indicating that the catalyst still activated the C–X bonds.

Lowering pH by addition of HCl had a strong effect on $e\text{ATRP}$ and drastically reduced the chain-end loss by cyclization. In reactions reported in Table 2, decreasing pH from 2.2 (the pH of 10% v/v MAA in water) to 0.9 led to an increased conversion of 96%, while dispersity decreased from 2.2 to <1.5 . Linear first-order kinetic plots and agreement between experimental and theoretical MW (Figure 1) proved a controlled polymerization. Figure 1e shows conversion and D as a function of pH; the best results were observed at pH 0.9.

In a solution containing 10% v/v MAA in water (pH = 2.2), $5.3 \times 10^{-3} \text{ M}$ (0.45%) of MAA is in the form of carboxylate anions. pH was lowered to decrease the concentration of

Table 1. Electrochemically Mediated ATRP of 10% v/v MAA in Water at $E_{\text{app}} = -0.20 \text{ V}$ vs SCE and $T = 25 \text{ }^\circ\text{C}$ ^a

entry	supporting electrolyte	t (h)	Q (C)	conv (%)	$k_p^{\text{app}b}$ (min^{-1})	$M_{n,\text{th}} \times 10^{-3}$	$M_{n,\text{app}} \times 10^{-3}$	I_{eff}^c	D
1	0.1 M NaBr	3	1.6	7	7.0×10^{-4}	1.3			
2	0.1 M NaCl	3	3.2	43	4.2×10^{-3}	8.0	15.6	0.53	2.5
3	0.3 M NaCl	3	1.7	65	7.0×10^{-3}	13.5	16.3	0.82	2.2

^aMeasured pH = 2.2. Conditions: $C_{\text{M}}:C_{\text{HEBiB}}:C_{\text{Cu}(\text{OTf})_2}:C_{\text{TPMA}} = 200:1:0.1:0.1$. $C_{\text{Cu}^{2+}} = 5.9 \times 10^{-4} \text{ M}$. $V_{\text{tot}} = 20 \text{ mL}$. ^bThe slope of the linear plot of $\ln(C_{\text{M}}^0/C_{\text{M}})$ vs t . ^cInitiation efficiency, $I_{\text{eff}} = M_{n,\text{th}}/M_{n,\text{app}}$.

Table 2. *e*ATRP and SARA ATRP of 10% v/v MAA in Water at Different pH and Target DP, $T = 25\text{ }^{\circ}\text{C}^a$

entry	pH	target DP	E_{app}^b (V)	t (h)	Q (C)	conv (%)	$k_p^{\text{app}c}$ (min^{-1})	$M_{n,\text{th}} \times 10^{-3}$	$M_{n,\text{app}} \times 10^{-3}$	I_{eff}^d	D
1 ^e	2.2 ^f	200	-0.20	3	1.7	66	0.007	13.6	16.3	0.83	2.18
2 ^e	1.4	200	-0.18	3	3.4	82	0.010	14.3	20.1	0.71	1.88
3	1.4	200	-0.18	3	3.0	83	0.011	14.5	21.8	0.67	1.72
4	1.1	200	-0.18	5	4.6	97	0.013	16.9	21.3	0.79	1.54
5	0.9	200	-0.18	4	4.7	96	0.015	16.8	21.8	0.77	1.49
6	0.6	200	-0.18	4	3.4	90	0.011	15.8	19.9	0.79	1.50
7 ^g	0.9	200	-0.18	4	3.2	96	0.014	16.8	18.0	0.93	1.42
8 ^g	0.9	500	-0.18	3	5.9	87	0.010	37.6	36.5	1.03	1.37
9 ^g	0.9	1000	-0.18	3	4.2	66	0.006	57.9	60.0	0.97	1.33
10 ^g	0.9	2000	-0.18	3	3.4	53	0.005	91.4	87.6	1.04	1.33
11 ^h	0.9	200		1.5		79	0.017	14.9	19.5	0.76	1.44
12 ^{h,j}	0.9	200		1.5		93	0.030	16.1	15.1	1.07	1.43
13 ^{h,j}	0.9	200		1.5		94	0.033	16.4	19.3	0.85	1.43

^apH was set by addition of HCl; NaCl was added to make $C_{\text{Cl}^-} = 0.3$ M. Unless otherwise stated, BiBA was the initiator. Other conditions: $C_{\text{M}}:C_{\text{RX}}:C_{\text{CuCl}_2}:C_{\text{TPMA}}:C_{\text{NaCl}} = 200:1:0.1:0.1:29$. $C_{\text{Cu}^{2+}} = 5.9 \times 10^{-4}$ M. $V_{\text{tot}} = 20$ mL. ^bvs SCE. ^cThe slope of the linear plot of $\ln(C_{\text{M}}^0/C_{\text{M}})$ vs t . ^d $M_{n,\text{th}}/M_{n,\text{app}}$. ^eRX = HEBiB. ^fpH of 10% v/v MAA in water. ^g $C_{\text{CuCl}_2}:C_{\text{TPMA}} = 1:4$. ^hConditions: $C_{\text{M}}:C_{\text{RX}}:C_{\text{CuCl}_2}:C_{\text{TPMA}}:C_{\text{NaCl}} = 200:1:0.01:0.4:29$; 10 cm Cu wire ($d = 1$ mm). Total $V = 5$ mL. pH was set by addition of HCl. ⁱ $C_{\text{NaCl}} = 0$ M. ^j $C_{\text{CuCl}_2} = C_{\text{NaCl}} = 0$ M. Cu wire used in a previous polymerization was recycled for this SARA ATRP, after rinsing with water.

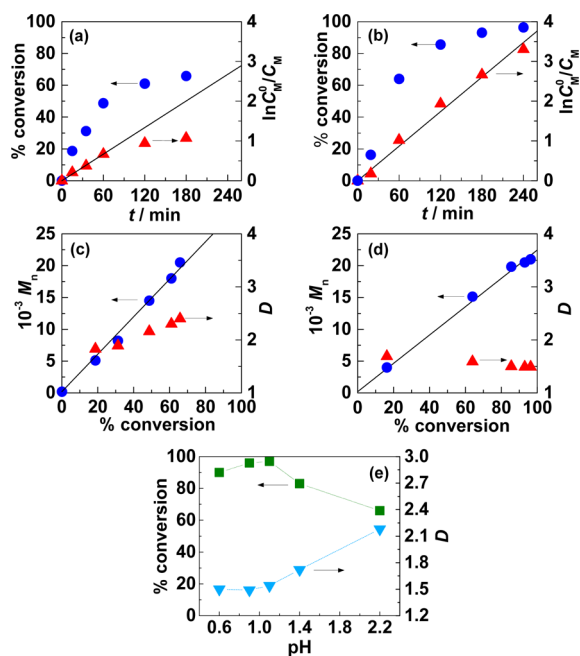


Figure 1. (a,b) First-order kinetic plots and (c,d) evolution of MW and dispersity (D) as a function of conversion for *e*ATRP of 10% v/v MAA in H_2O at $E_{\text{app}} = -0.18$ V vs SCE, at pH 2.2 (a,c) or at pH 0.9 (b,d). NaCl was added to make $C_{\text{Cl}^-} = 0.3$ M. Conditions: $C_{\text{M}}:C_{\text{RX}}:C_{\text{CuCl}_2}:C_{\text{TPMA}} = 200:1:0.1:0.1$, $T = 25\text{ }^{\circ}\text{C}$. (e) Conversion (green squares) and D (blue triangles) in *e*ATRP experiments as a function of pH.

carboxylate anions to 0.02%, since they are stronger nucleophiles than the carboxylic acid, thus decreasing the negative impact of the lactone formation at the chain end.

Both HEBiB and BiBA, which better mimics the PMAA chain end, efficiently initiated the polymerization. Regarding the catalyst, a ligand-to-copper ratio of 4:1 provided faster reactions and better control than a ratio of 1:1 (entries 5 and 8). Excess ligand compensated for the protonation of TPMA at pH 0.9 (see quantitative calculations in the SI).

E_{app} was used to modulate polymerization rate. In the *e*ATRP of MAA at pH 0.9, $E_{\text{app}} - E_{1/2} = (-0.18 + 0.06)$ V = -0.12 V was applied (entry 5). Under such conditions, Cu^{II} reduction was limited by mass transport, and polymerization reached the highest rate.¹⁸ Consequently, the contribution of lactone formation to chain termination was minimized.

Synthesis of high-MW PMAA was carried out by lowering the initiator concentration (entries 8–11). Figure S13 shows that MW increased fairly linearly with conversion and that final M_n closely matched the theoretical value (with $D \leq 1.42$). When targeting DP = 2000, a polymer with DP > 1000 and $D = 1.33$ was synthesized in 3 h.

Polymerization was also carried out by SARA ATRP in the presence of Cu wire. SARA ATRP was faster than *e*ATRP, with a similar level of control (entries 11–13 and Figure S14). The setup was further simplified by using HCl as the only source of Cl^- to prevent dissociation of $[\text{Cl-Cu}^{\text{II}}\text{L}]^+$ (no NaCl, entry 12). Cu wire was recycled by simple rinsing with water, without any activation procedure: the acidic solution easily dissolved the oxidized Cu species from the surface, activating Cu^0 and providing Cu^{II} , which triggered comproportionation and efficient polymerization (entry 13).

A concentration range between 5% and 25% MAA in water was suitable for the polymerization by both SARA ATRP and *e*ATRP (Table S2 and Figure S15).

To verify the living character of the process, the applied potential was used to repetitively switch the system between active and dormant states. This was achieved by cycling E_{app} between -0.2 and $+0.8$ V vs SCE (Figure 2). At $E = -0.2$ V, polymerization was activated by converting Cu^{II} to Cu^{I} at the electrode. In contrast, at $E = 0.8$ V, the activator was quenched by rapidly converting Cu^{I} to Cu^{II} and transforming the propagating radicals to dormant species (Scheme 1). This electrochemical ON/OFF switch was applied four times, increasing the monomer conversion to 22, 40, 49, and 59% during the active periods. Negligible conversion was observed during the OFF periods. M_n steadily increased during the ON periods, while no low-MW polymers were detected (Figure 2b). These observations demonstrate the living character of the polymerization: efficient re-initiation of chain ends resulted

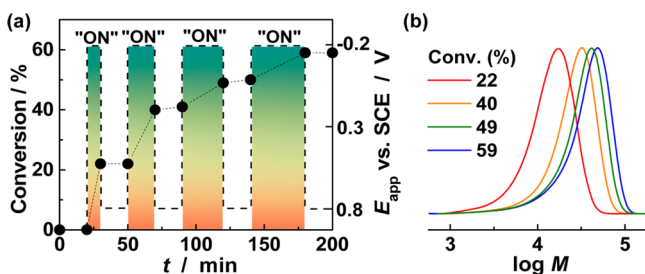


Figure 2. (a) Variation of conversion (full circles) and applied potential (dashed lines) with time during eATRP of MAA (no potential was applied in the first 20 min). (b) Evolution of MW with monomer conversion, after each step at $E_{\text{app}} = -0.2$ V vs SCE. Conditions: $C_M:C_{\text{CuCl}_2}:C_{\text{TPMA}}:C_{\text{NaCl}} = 200:1:0.1:0.4:29$, $T = 25$ °C. pH 0.9 was set by addition of HCl.

from minor termination and adequate preservation of chain-end functionality.

In conclusion, 2D NMR and FT-IR showed that the predominant termination of the MAA polymer chains was due to an intramolecular cyclization reaction, rather than biradical termination. Three approaches significantly increased conversion and improved control over ATRP of MAA: (i) using Cl as chain-end halogen, (ii) lowering the pH to 0.9, and (iii) accelerating the polymerization rate. MAA was polymerized using 500 ppm of copper by both eATRP and SARA ATRP, with adequate control over dispersity ($D < 1.5$) and M_n in agreement with theoretical values. The reaction was relatively fast (96% conversion in 4 h, 25 °C) with inexpensive and nontoxic reagents (NaCl, diluted HCl, water). The living/controlled nature of the process was demonstrated by linear first-order kinetics, linear increase of MW with monomer conversion, and the possibility to completely reactivate the polymerization by repetitively varying the applied potential.

The use of Cu/TPMA as an efficient catalyst under acidic conditions, although usually considered harmful for any ATRP process, resulted in the successful direct synthesis of an acidic polymer in water. This result overcomes one of the biggest limitations of ATRP and proves that water is an excellent solvent for ATRP of polar monomers.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b01935.

Experimental section, CVs, chronoamperometry, and detailed 2D and ^1H NMR spectra of the chain end, including Figures S1–S15, Tables S1 and S2, and Schemes S1 and S2 (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*abdirisak.ahmedisse@unipd.it
 *armando.gennaro@unipd.it
 *km3b@andrew.cmu.edu

Notes

The authors declare no competing financial interest.

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