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Atom Transfer Radical Polymerization of Acrylic and Methacrylic Acids: Preparation of Acidic Polymers with Various Architectures

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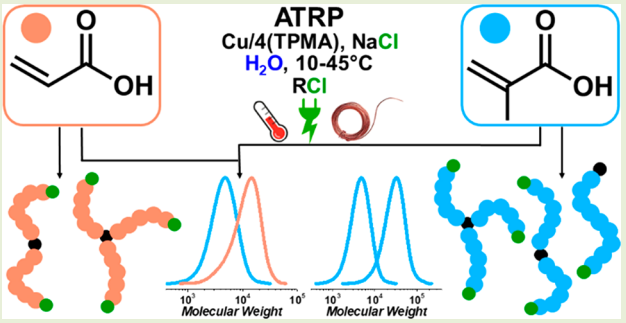
ABSTRACT: The preparation of poly(acrylic acid) (PAA) with tailored architecture and morphology is important for the design of advanced polymer materials. Cu-catalyzed atom transfer radical polymerization (ATRP) of AA is challenging due to the tendency of dormant chains to undergo an intramolecular lactonization reaction with consequent loss of chain-end functionalities, as previously reported for ATRP of methacrylic acid (MAA). In addition, AA can coordinate to the Cu catalyst. Moreover, the lower ATRP reactivity of AA relative to MAA enhances side reactions during polymerizations. These issues were overcome by adjusting the composition of the catalytic system, the polymerization setup, and the initiator nature. AA conversion >70−80% was obtained in 5 h, producing PAA with $Đ$ ≈1.4. Multifunctional water-soluble initiators provided PAA and PMAA with telechelic and star-shaped architectures. Block copolymers of MAA and AA confirmed the retention of chain-end functionalities during ATRPs.



Poly(acrylic acid) (PAA) is a fundamental component of commercial adhesives, detergents, superabsorbents, and coatings. Vast industrial and academic research has focused on the utilization of acrylic acid for stimuli-responsive materials, biocompatible hydrogels and brushes, and binders or membranes for energy devices.[1−4] Tailoring the morphology and topology of PAA can lead to materials with improved and tunable properties. However, PAA is largely synthesized through free radical polymerization with limited architectural control.[5,6] Synthetic challenges are associated with the high propagation rate constant of AA (k_p ∼10^5 L mol^{-1} s^{-1}, for 20 wt % AA in H_2O), which strongly depends on the solution pH and monomer and polymer concentration, and can result in enhanced backbiting and gelation.[7−10]

Reversible deactivation radical polymerization (RDRP) methods provide exceptional control over the molecular weight (MW) and dispersity ($Đ$) of a large variety of monomers. However, only a few reports address the controlled polymerization of acidic monomers and particularly AA. Nitroxide mediated polymerization (NMP),[11,12] reversible addition−fragmentation chain-transfer (RAFT) polymerization,[13−18] reverse iodine transfer polymerization (RITP),[19] and other techniques[20−22] provided moderately controllable PAA synthesis, yet required high temperatures, long reaction times, and/or expensive and not readily available catalytic or chain-transfer systems. Thus, the most common way to prepare well-defined PAA is via RDRP of *tert*-butyl acrylate followed by deprotection of the *tert*-butyl group.[23−25] The development of a procedure to prepare well-defined homo- and copolymers of AA with commercially available materials under mild conditions remains highly desirable.

Among RDRP methods, atom transfer radical polymerization (ATRP) has been considered incompatible with acidic monomers, due to the tendency of $-COO^-$ groups to chelate to Cu complexes used as ATRP catalysts and/or protonation of Cu ligands, inhibiting the catalytic activity.[26−29] However, it was recently demonstrated that the main obstacle to aqueous ATRP of methacrylic acid (MAA) is an intramolecular cyclization reaction affecting PMAA chains, leading to loss of chain end functionalities and ultimately a halt of the polymerization.[30] ATRP is based on the activation/deactivation equilibrium between propagating radicals and halogen (X)-capped dormant species, regulated by a Cu/L catalyst (L = polydentate amine ligand) in the form of $[Cu^IL]^+$ activator and $[X\text{-}Cu^{II}L]^+$ deactivator (Scheme 1a).[31] In the Cu-catalyzed ATRP of MAA, PMAA-X dormant chains can undergo an intramolecular lactonization reaction to form a 5-membered ring (Scheme 1b). This side reaction was minimized by (i) switching from C−Br to C−Cl chain ends; (ii) decreasing the solution pH, and (iii) enhancing the polymerization rate.[30] In

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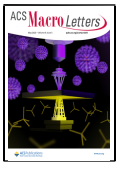

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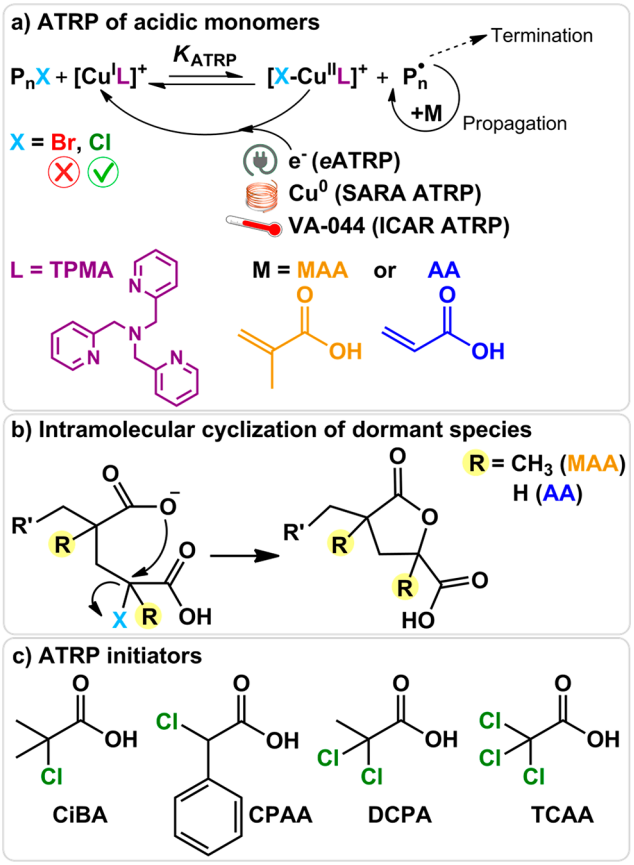
Scheme 1. (a) Mechanism of ATRP with Activators Regeneration Used in This Work; (b) Proposed Mechanism of Intramolecular Lactonization; and (c) Employed ATRP Initiators



addition, employing TPMA (tris(2-pyridylmethyl)amine) as ligand and using excess of Cl^- ensured sufficient catalyst stability at low pH and prevented the dissociation of the [Cl–Cu^{II}TPMA]$^+$ deactivator, respectively.[30,32,33] Alternatively, the side-chain lactonization appeared negligible in Fe-catalyzed and organocatalyzed ATRP of MAA, however these techniques present more limitations than conventional Cu-catalyzed ATRP.[34,35]

Well-controlled Cu-catalyzed polymerization of MAA was obtained by electrochemically mediated ATRP (*e*ATRP) and supplemental activator and reducing agent (SARA) ATRP (Scheme 1a). These techniques used an applied potential/current or a metallic Cu wire, respectively, to continuously regenerate the [Cu^IL]$^+$ activator from the Cu^{II} species that accumulated because of unavoidable terminations.[36−38] Thus, polymerizations were performed at low catalyst loading (<1000 ppm) and under mild conditions.

Herein, we first sought to define the conditions for aqueous ATRP of AA by investigating the behavior of the Cu catalyst in the presence of AA. Cyclic voltammetry (CV) of the [Cl–Cu^{II}TPMA]$^+$ complex indicated that the monomer can coordinate to the catalyst. The quasi-reversible peak couple observed in pure water became irreversible upon addition of even a small amount of AA (Figure S1, Supporting Information), suggesting that the monomer could bind to the electro-generated [Cu^ITPMA]$^+$, thus preventing its reoxidation to [Cl–Cu^{II}TPMA]$^+$.[39] Conversely, addition of MAA did not modify the voltammetric response of the catalyst, indicating negligible monomer coordination.[30] In order to diminish the complexation between AA and the catalyst, a 4-fold excess of TPMA relative to Cu was employed in polymerizations.

The ATRP equilibrium constant, K_{ATRP}, for AA should be lower than K_{ATRP} for MAA, due to the lower bond dissociation energy of secondary alkyl halides, likely resulting in slower polymerizations.[40,41] The presence of a large amount of halide salt, needed to stabilize the ATRP deactivator in aqueous media, can further slowdown the polymerization due to the formation of inactive [XCu^IL] species and relative decrease in the concentration of active catalyst [Cu^IL]$^+$.[42] Thus, to increase the polymerization rate, the concentration of halide salt was set to ∼40 equiv to Cu, much lower than for MAA polymerizations (∼500 equiv). Furthermore, *e*ATRP allows for increasing the polymerization rate by (i) applying a potential (E_{app}) value more negative than the cathodic peak potential (E_{pc}) of the catalyst (E_{app} = −0.3 V vs SCE = E_{pc} − 0.06 V); (ii) using two Pt meshes as working electrode to enhance surface-to-volume ratio (∼2 cm^2/mL of solution, based on the geometrical surface area), promoting a more effective activator regeneration.[38]

Nevertheless, a first *e*ATRP of AA in water with an alkyl bromide initiator and 40 equiv of NaBr to Cu/TPMA (1/4) resulted in 10% conversion of AA in 30 min, after which the polymerization stopped (Figure S2), suggesting that all chains were terminated. The obtained polymer had high dispersity

Table 1. Effect of Initiator (RCl) Nature, Temperature, and Degree of Polymerization on Aqueous *e*ATRP of AA[a]

entry	RCl	T (°C)	AA (vol %)	DP	conversion[b] (%)	$k_{p,app}$[c] (h^{-1})	$M_{n,th}$[d] (×10^{-3})	M_n[e] (×10^{-3})	$Đ$
1	CiBA	25	10	175	56	0.17	7.1	12.8	1.76
2	CPAA	25	10	175	56	0.19	7.1	17.5	1.72
3	DCPA	25	10	175	81	0.37	10.3	15.8	1.43
4[f]	DCPA	25	10	175	92	0.60	11.6	20.3	1.45
5	TCAA	25	10	175	87	0.44	11.0	17.9	1.36
6	TCAA	10	10	175	92[g]	0.23	11.6	20.0	1.38
7	TCAA	40	10	175	73[h]	0.55	9.3	16.5	1.39
8	TCAA	25	5	88	78	0.35	5.1	8.5	1.37
9	TCAA	25	25	434	81	0.39	25.5	30.2	1.38
10	TCAA	25	50	867	38	0.12	24.0	49.8	1.41

[a]General conditions: $C_{RCl}/C_{Cu^{II}Cl_2}/C_{TPMA}/C_{Cl^-}$ = 1/0.1/0.4/4. $C_{Cu^{2+}}$ = 8.3 × 10^{-4} M. E_{app} = −0.3 V vs SCE, pH ≈ 2, V_{TOT} = 15 mL. [b]After 5 h, unless otherwise stated. [c]Slope of $\ln(C^0_{AA}/C_{AA})$ vs time. [d]$M_{n,th} = MW_{RCl}$ + conv. × DP × MW_{AA}. [e]Measured by GPC (eluent: 0.1 M Na_2HPO_4 in H_2O; calibration: poly(sodium methacrylate) standards). [f]$C_{Cu^{II}Cl_2}/C_{Cl^-}$ = 0.1/1. [g]After 12 h. [h]After 3 h.

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(Table S1). By replacing NaBr with NaCl the conversion steadily increased, reaching 50% in 3 h, and then it remained unchanged. Despite the polymerization being poorly controlled, the improved conversion suggests that PAA-X dormant species could undergo a similar intramolecular lactonization reaction (Scheme 1b) as PMAA-X dormant chains, which proceeded faster when X = Br.[30]

To avoid the formation of C−Br chain ends prone to lactonization, 2-chloroisobutyric acid (CiBA, Scheme 1c) was employed as initiator. The system reached 56% monomer conversion in 5 h (Table 1, Entry 1), but the control remained limited. To further suppress the lactonization, HCl was added to lower the solution pH to 1.4 and 0.9 (which completely converted COO^- to the less nucleophilic COOH). However, this resulted in slower polymerizations with no improved control (Table S2). The lower polymerization rates were attributed to the lower catalyst activity at strongly acidic pH. Indeed, CV showed a shift in E_{pc} of $[Cl-Cu^{II}TPMA]^+$ to more positive values with decreasing pH (Figure S3), corresponding to a decrease in the catalyst activity.[33] Thus, subsequent polymerizations were performed without modifying the solution pH (pH ≈ 2).

In order to improve the initiation efficiency (i.e., the match between theoretical and measured MW), α-chlorophenylacetic acid (CPAA, Scheme 1c) was used as an initiator with much higher reactivity than CiBA, due to the strongly activating phenyl-acetic group. However, both the initiation efficiency and overall control were limited (Table 1, Entry 2). Conversely, multifunctional initiators (Scheme 1c) such as 2,2-dichloropropionic acid (DCPA) and trichloroacetic acid (TCAA) enabled faster and better controlled polymerizations (Table 1, Entries 3, 5). The *e*ATRP initiated by DCPA reached 81% monomer conversion in 5 h, giving PAA with $Đ$ = 1.43, while by using TCAA the polymerization reached 87% conversion in 5 h, giving PAA with $Đ$ = 1.36.

These initiators provided polymers with different architectures (Scheme S1): DCPA can initiate two chains per molecule, providing access to telechelic polymers, whereas TCAA can give three-arm star polymers.

The increase in the apparent polymerization rate ($k_{p,app}$) by switching from mono- to di- and trifunctional initiators supports that all C−Cl bonds in DCPA and TCAA molecules were activated. It should be noticed that PAA MWs have uncertainty due to the use of poly(sodium methacrylate) samples as calibration standards for the gel permeation chromatography (GPC), and different hydrodynamic volume between stars and linear chains.[43]

As expected, reducing the concentration of chloride salt to 10 equiv relative to Cu/TPMA (1/4) resulted in faster polymerization (Table 1, Entry 4), although the semilogarithmic kinetic plots showed larger deviation from linearity (Figure S5) and the polymer dispersity slightly increased. By increasing the temperature from 25 to 40 °C, the polymerization was about twice as fast, but strongly slowed down after reaching 73% monomer conversion in 3 h (Table 1, Entries 5−7). This behavior was attributed to enhanced side reactions at higher temperature. Conversely, by decreasing the temperature to 10 °C, the polymerization reached 92% monomer conversion within 12 h. Various degrees of polymerization (DPs) were targeted by changing the monomer loading while keeping constant the concentration of TCAA initiator and other components (Table 1, Entries 5, 8−10, and Figure S6). *e*ATRPs of 5, 10, and 25 vol % AA proceeded at similar rates, giving PAA with MW ranging from 8000 to 30 000 and $Đ$ ≈ 1.37. When increasing the monomer loading to 50 vol %, the polymerization was much slower due to the strong increase in viscosity, which likely hindered the mass transport of Cu complexes to the electrode, resulting in decreased control.[44]

The effect of the catalyst loading on the *e*ATRP of 10 vol % AA and DCPA as initiator was analyzed (Table S3 and Figure 1). Typically, the catalyst loading affects the rate of *e*ATRP,

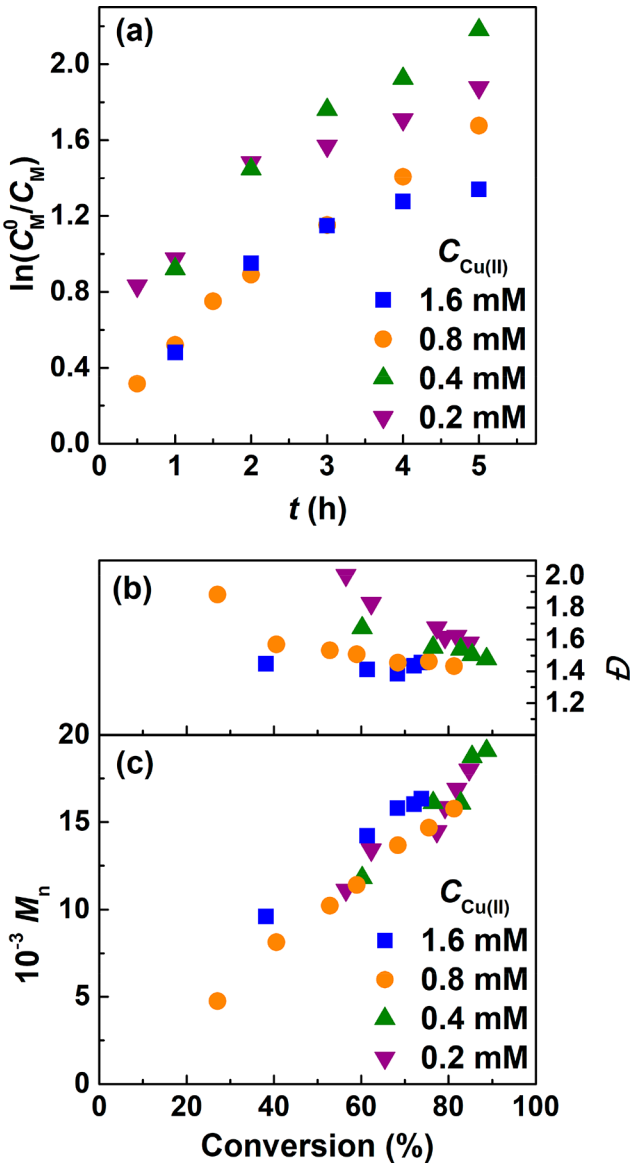

Figure 1. *e*ATRP of AA 10 vol % in H_2O with different catalyst loadings: (a) semilogarithmic kinetic plots, (b) dispersity, and (c) MW evolution vs conversion. Polymerization conditions: C_{AA}/C_{DCPA} = 175/1. C_{DCPA} = 8.3 × 10^{-3} M, $C_{Cu^{II}Cl_2}/C_{TPMA}/C_{Cl^-}$ = 1/4/40. WE area ca. 30 cm^2. V_{tot} = 15 mL, T = 25 °C.

which increases with the square root of Cu concentration.[38] However, the polymerizations of AA accelerated when decreasing the catalyst loading from 1.6 mM to 0.4 mM. The latter, corresponding to 275 ppm of Cu (relative to the molar concentration of AA), provided acceptable control, and 89% AA conversion was reached after 5 h. Further decreasing C_{Cu} to 0.2 mM led to a slower polymerization, producing PAA

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with higher dispersity, likely because of the insufficient amount of $[Cl-Cu^{II}TPMA]^+$ deactivator.

Initiator for continuous activator regeneration (ICAR) ATRP of AA was also performed, and the effects of target DP and Cu loading were studied (Table S4). In ICAR ATRP, a conventional thermally activated radical initiator provides radicals for the continuous regeneration of $[Cu^IL]^+$.[31,45] 2,2′-Azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044) was used as water-soluble radical initiator at T = 45 °C, and in the presence of DCPA as ATRP initiator. The ICAR ATRP of 5 vol % AA reached 60% monomer conversion in 3.5 h, giving PAA with $Đ$ = 1.34 (Table S4, Entry 1). The polymerization rate decreased with increasing the monomer content to 10 and 25 vol %, but the control was maintained. In ICAR ATRP, the polymerization rate should depend not on the catalyst loading, but on the amount of radical initiator. The polymerization of 25 vol % AA accelerated with decreasing the catalyst loading from 0.8 mM to 0.2 mM (Table S4, Entries 3–5). By using C_{Cu} = 0.8 mM, the polymerization was very slow, and only 29% AA conversion was reached after 16 h with poor control over the chain growth. Decreasing C_{Cu} to 0.4 mM enabled the achievement of 54% AA conversion in 8 h, and PAA with $Đ$ = 1.47. Further decreasing C_{Cu} to 0.2 mM resulted in faster polymerization, but slightly higher PAA dispersity.

The increase in polymerization rate with reduction in catalyst loading may indicate that the Cu complex is involved in side reactions that slow down the polymerization, such as Cu-catalyzed radical termination (CRT), which proceeds through the formation of an organometallic intermediate[46,47] or chain-end lactonization. Negligible lactonization was observed in Fe-catalyzed ATRP of MAA, further suggesting that the catalyst nature has an effect on this side reaction.[34] Mechanistic studies are required to better understand and manipulate the cyclization pathway.

After exploring the ATRP of AA, we tested the effect of different initiators on ATRP of MAA (Figure 2). Previously, only 2-bromoisobutyric acid (BiBA), which mimics PMAA chain ends, was reported as an efficient initiator for *e*ATRP and SARA ATRP of MAA.[30] Alkyl chloride initiators were tested herein to eliminate Br^- from the system. When CiBA was used as initiator, the *e*ATRP of MAA at pH = 0.9 was slower than that by using BiBA under similar conditions, and the initiation efficiency was poor (Table 2, Entry 1), likely because CiBA (C–Cl bond) is less reactive than BiBA (C–Br bond). The more active CPAA ensured efficient initiation of all chains and fast polymerization, but the obtained PMAA had high dispersity, $Đ$ = 1.6 (Table 2, Entry 2). The multifunctional initiators DCPA and TCAA enabled good initiation efficiency and MAA conversion >98% in 4 h (Table 2, Entries 3, 5), giving telechelic and three-arm star polymers (Figure S4) with $Đ$ < 1.4. As observed for AA, $k_{p,app}$ increased with an increasing number of C–Cl bonds in the initiating molecules. Good control was maintained on *e*ATRP of MAA initiated by TCAA upon increasing the target DP from 200 to 600, obtaining PMAA with MW ≈ 43 000 and $Đ$ = 1.32 (Table 2, Entry 6). Moreover, SARA ATRP of MAA initiated by DCPA or TCAA was faster than the corresponding *e*ATRP, while giving PMAA with even lower dispersity (Table 2, Entries 4, 7).

Finally, block copolymers of acidic monomers were prepared by SARA and *e*ATRP (Table S5), proving the retention of chain end functionality during polymerizations, and further demonstrating the synthesis of polymers with different architectures. PMAA-Cl macroinitiator (M_n = 3800, $Đ$ = 1.36) was prepared by *e*ATRP initiated by DCPA, then precipitated in diethyl ether, purified, and dried under vacuum overnight. SARA ATRP was then used for the chain extension of PMAA-Cl with MAA, with different target DPs. For target DP = 200, the system reached 93% monomer conversion in 2 h, yielding polymer with M_n = 24 000 and $Đ$ = 1.41. The GPC traces showed a clear shift to higher MW values, indicating efficient reinitiation of PMAA chains (Figure 3a). The clean trace shift was evident also when targeting DP = 420 (Figure S7).

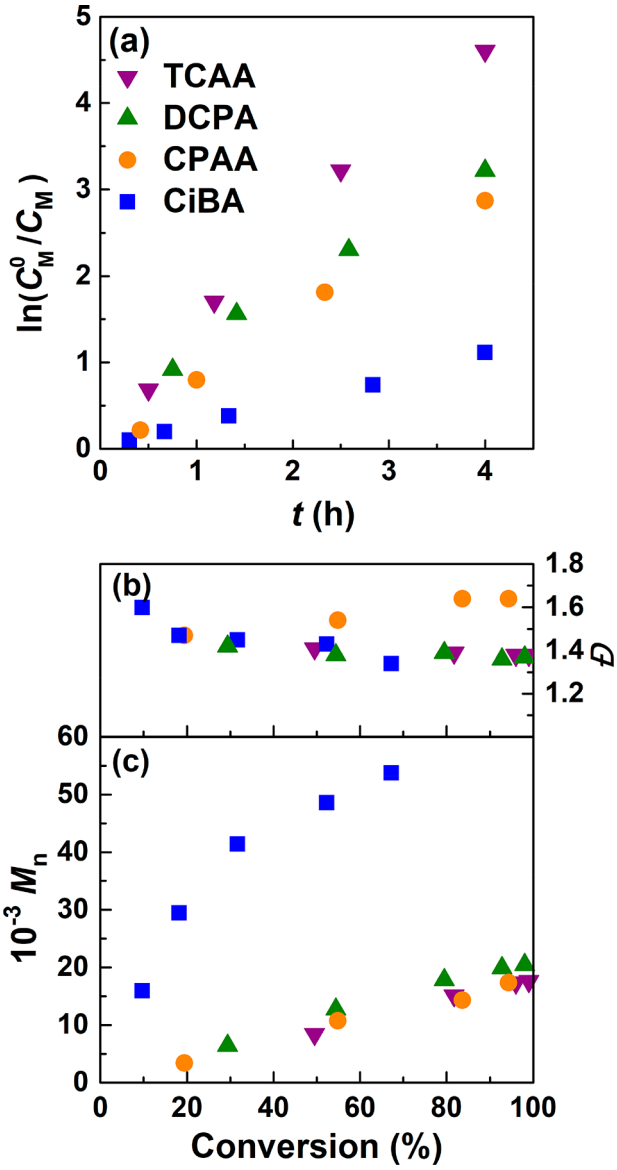

Figure 2. *e*ATRP of 10 vol % MAA in H_2O with different initiators: (a) semilogarithmic kinetic plots, (b) dispersity, and (c) MW evolution vs conversion. E_{app} = −0.18 V vs SCE at pH 0.9, $C_{MAA}/C_{RCl}/C_{Cu^{II}Cl_2}/C_{TPMA}/C_{Cl^-}$ = 200/1/0.1/0.4/51, $C_{Cl^-} = C_{HCl} + C_{NaCl}$ = 0.3 M, T = 25 °C.

Chain extension of PMAA-Cl was also performed by *e*ATRP of either MAA (Figure S8) or AA. However, when using AA as second monomer, it was necessary to stop the polymerization at lower conversion, to retain narrow MW distribution in the copolymer. This behavior could be attributed to the relatively low reactivity of AA as well as to the tendency of AA to coordinate to the Cu^I species. Both these phenomena

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Table 2. Effect of the Initiator Nature on *e*ATRP and SARA ATRP of 10 vol% MAA in Water at pH 0.9, T = 25 °C[a]

entry	technique	RCl	t (h)	conversion (%)	$k_{p,app}$ (h^{-1})	$M_{n,th} \times 10^{-3}$	$M_n \times 10^{-3}$	$Đ$
1	*e*ATRP	CiBA	4	67	0.30	11.8	53.8	1.34
2	*e*ATRP	CPAA	4	94	0.62	16.4	17.4	1.64
3	*e*ATRP	DCPA	4	98	1.02	17.1	20.5	1.37
4	SARA-ATRP	DCPA	2.5	96	1.38	16.8	23.7	1.25
5	*e*ATRP	TCAA	4	99	1.20	17.0	17.6	1.38
6[b]	*e*ATRP	TCAA	3	95	1.02	49.2	42.9	1.32
7	SARA-ATRP	TCAA	1.2	94	2.58	16.3	18.9	1.33

[a]General conditions: pH was set by addition of HCl; NaCl was added to set total $C_{Cl^-} = C_{HCl} + C_{NaCl}$ = 0.3 M. *e*ATRP conditions: $C_{MAA}/C_{RCl}/C_{Cu^{II}Cl_2}/C_{TPMA}/C_{Cl^-}$ = 200/1/0.1/0.4/51, $C_{Cu^{2+}} = 5.9 \times 10^{-4}$ M, V_{TOT} = 15 mL, E_{app} = −0.18 V vs SCE. SARA ATRP conditions: $C_{MAA}/C_{RCl}/C_{Cu^{II}Cl_2}/C_{TPMA}/C_{Cl^-}$ = 200/1/0.01/0.3/51, V_{TOT} = 5 mL, Cu wire l = 10 cm, d = 1 mm. [b]C_{MAA}/C_{TCAA} = 200/0.333 (DP = 600).

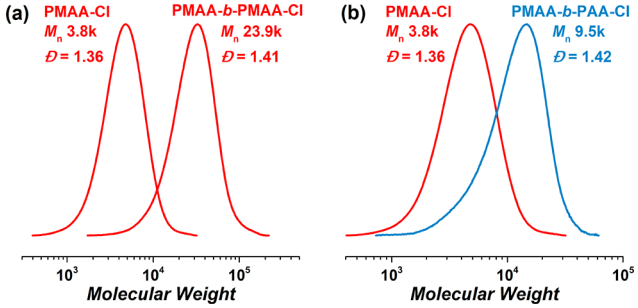

Figure 3. Chain extension of PMAA-Cl macroinitiator via (a) SARA-ATRP of 10 vol% MAA in H_2O, pH = 0.9, $C_{MAA}/C_{PMAA\text{-}Cl}/C_{Cu^{II}Cl_2}/C_{TPMA}/C_{Cl^-}$ = 200/1/0.01/0.4/14, Cu wire l = 10 cm, d = 1 mm; MAA conversion = 93% in 2 h. (b) *e*ATRP of 10 vol% AA in H_2O, pH ≈ 2, $C_{AA}/C_{PMAA\text{-}Cl}/C_{Cu^{II}Cl_2}/C_{TPMA}/C_{Cl^-}$ = 200/1/0.1/0.4/4, E_{app} = −0.3 V vs SCE; AA conversion = 40% in 1.5 h. The GPC traces were recorded using 0.1 M Na_2HPO_4 in H_2O as eluent and poly(sodium methacrylate) standards for calibration.

contributed to a relatively slow polymerization, where side reactions such as chain-end lactonization were more prominent. Nevertheless, PMAA-*b*-PAA with MW matching the theoretical value and $Đ$ = 1.42 was obtained upon stopping the *e*ATRP after 90 min, at 40% AA conversion (Figure 3b).

In summary, well-controlled polymerization of acrylic acid was achieved by Cu-catalyzed ATRP in water. Growing polymer chains tend to terminate via an intramolecular cyclization reaction, similar to ATRP of MAA. The ATRP of AA is additionally hampered by (i) the coordination of AA to the Cu catalyst, and (ii) the lower ATRP reactivity of AA compared to MAA. Therefore, the concentration of Cl^- and the polymerization setup were optimized to find a compromise between the rate of polymerization and the contribution of side reactions. The reported polymerizations used commercially available catalyst and initiators under mild conditions. The continuous supply of ATRP activator to the system was ensured by various stimuli, demonstrating the versatility of the process and enhancing the sustainability of the polymerization by using electricity as a trigger.

By employing multifunctional alkyl chloride initiators, monomer conversions >70−80% were achieved within 5 h, obtaining PAA with $Đ$ = 1.36−1.45. The same initiators were also suitable for ATRP of MAA, reaching >95% conversion in less than 4 h and yielding PMAA with $Đ$ = 1.25−1.38. The polychlorinated initiators provided telechelic and star-shaped polymers. Moreover, block copolymers were prepared by chain extension of a PMAA macroinitiator with either MAA or AA, confirming the good retention of chain-end functionality. In conclusion, well-defined polymer architecture of acidic monomers in water can be prepared by Cu-catalyzed ATRP by employing C−Cl chain ends and TPMA as ligand, and by promoting faster polymerization to minimize side reactions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.0c00246.

Synthetic procedures, additional polymerization data, and electrochemical characterization (PDF)

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Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

AA, acrylic acid; ATRP, atom transfer radical polymerization; BiBA, 2-bromoisobutyric acid; CiBA, 2-chloroisobutyric acid; CPAA, α-chlorophenylacetic acid; DCPA, 2,2-dichloropropionic acid; GPC, gel permeation chromatography; *e*ATRP, electrochemically mediated atom transfer radical polymerization; ICAR, initiator for continuous activator regeneration; MAA, methacrylic acid; RDRP, reversible deactivation radical polymerization; SARA, supplemental activator and reducing agent; SCE, saturated calomel electrode; TCAA, trichloroacetic acid; TPMA, tris(2-pyridylmethyl)amine; VA-044, 2,2′-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride.

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