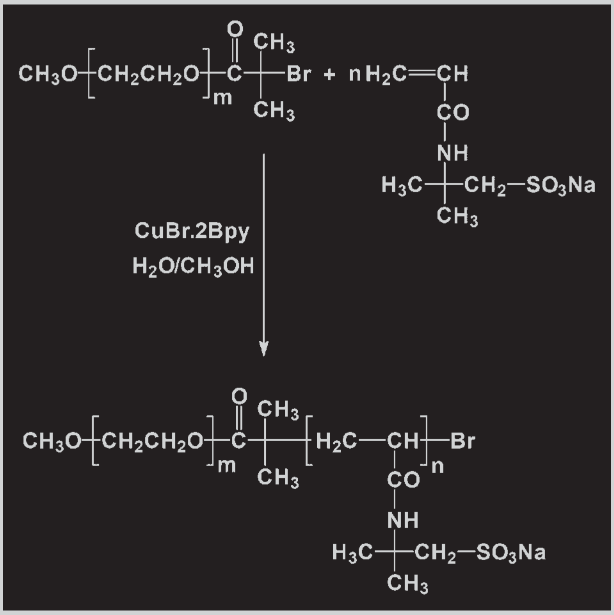
**Summary:** Well-defined poly[(ethylene oxide)-*block*-(sodium 2-acrylamido-2-methyl-1-propane sulfonate)] diblock copolymers [P(EO$_m$-*b*-AMPS$_n$)], have been obtained by water-based ATRP using α-methoxy-ω-(2-methylbromoisobutyrate) poly(ethylene oxide)s (MeO-P[EO]$_m$-Br$^i$B with $m$ ranging from 12 to 113) and CuBr · 2Bpy (Bpy for 2,2′-bipyridyl) as macroinitiator and catalytic complex, respectively. Compared to direct polymerization in water, it has been demonstrated that the water/methanol (3:1, v/v) mixture is better suited for predicting the final number-average molar mass from the initial monomer-to-macroinitiator molar ratio and achieving a quite narrow polydispersity, even at high monomer conversion ($\overline{M}_w/\overline{M}_n \approx 1.4$ at 80% conversion). The effect of temperature, solvent mixture composition and addition of NaCl salt on the polymerization rate and extent of control over the copolymer molecular parameters have been highlighted as well.



# Preparation of Well-Defined Poly[(ethylene oxide)-*block*-(sodium 2-acrylamido-2-methyl-1-propane sulfonate)] Diblock Copolymers by Water-Based Atom Transfer Radical Polymerization

*Dilyana Paneva,*[1,2] *Laetitia Mespouille,*[2] *Nevena Manolova,*[1] *Philippe Degée,*[2] *Iliya Rashkov,*[1] *Philippe Dubois**[2]

[1] Laboratory of Bioactive Polymers, Institute of Polymers, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
[2] Laboratory of Polymeric and Composite Materials, University of Mons-Hainaut, Place du Parc 20, B-7000 Mons, Belgium
E-mail: philippe.dubois@umh.ac.be

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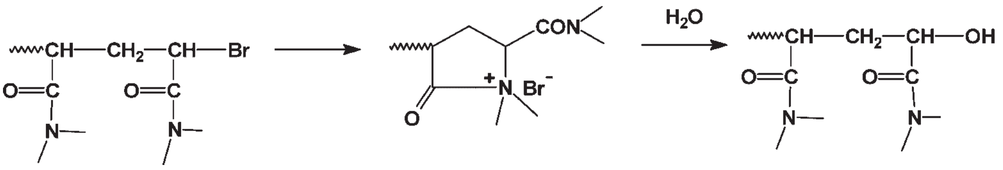
**Keywords:** atom transfer radical polymerization (ATRP); diblock copolymers; poly[(ethylene oxide)-*block*-(sodium 2-acrylamido-2-methyl-1-propane sulfonate)] [P(EO$_m$-*b*-AMPS$_n$)]; water-based ATRP

## Introduction

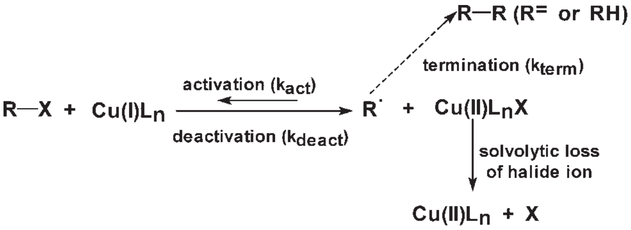
Sodium 2-acrylamido-2-methyl-1-propane sulfonate (AMPS) based (co)polymers are used in a wide range of applications such as detergents, thickeners, paper-coatings, and dental adhesives but they have also gained interest due to their anticoagulant properties[1] and their ability to improve the compatibility of polymers with blood.[2,3] Similarly, poly(ethylene oxide) (PEO) segments are well-known to highly reduce non-specific interactions with blood proteins by a steric repulsion mechanism and might increase further blood compatibility of AMPS-based copolymers.[4] In 2001, the preparation of well-defined PAMPS homopolymer and block copolymers with sodium 3-acrylamido-3-methylbutanoate has been achieved by reversible addition-fragmentation chain transfer (RAFT) polymerization using 4,4′-azobis(4-cyanopentanoic acid) and 4-cyanopentanoic acid dithiobenzoate as initiator and chain transfer agent, respectively, at 70 °C in water.[5] The solution pH was adjusted at 9.6. As far as water-based atom transfer radical



Scheme 1. Side termination reaction in water-based ATRP of acrylamido monomers-conversion of bromide active sides in hydroxyl groups.

polymerization (ATRP) is concerned, the controlled polymerization of (meth)acrylamido monomers is problematic.[6–8] The lack of control in ATRP of (meth)acrylamides has been attributed to the loss of bromide active sites through a cyclization reaction involving the nucleophilic displacement of bromine atom by the penultimate amide nitrogen atom, followed by the hydrolysis of the cyclic intermediate leading to inactive hydroxyl end-capped polymer chains (Scheme 1).[7] In addition to the usual termination by disproportion and recombination, this specific termination reaction is favored by the slow deactivation rate (Scheme 2) in water-based ATRP of (meth)acrylamides which can be explained by both the complex formation between copper-based catalyst and amide groups[6] and the solvolytic loss of the halide ion from the deactivating higher oxidation state metal complex (Scheme 2).[9] Masci et al. first succeeded in controlling the water-based ATRP of *N*-isopropylacrylamide using ethyl 2-chloropropionate and CuCl · tris(2-dimethylaminoethyl)amine (CuCl · $Me_6$TREN) as initiator and catalytic complex, respectively, in dimethylformamide/water (1:1, v/v) mixtures at 20 °C.[10] Substituting AMPS for non-ionic acrylamides requires the addition of $CuCl_2$ to the catalytic system to partially control the homopolymerization of AMPS and its block copolymerization. Indeed, an upward curvature of the first-order kinetic plot was observed as a result of Cu(II) complex formation with PAMPS reducing the concentration of deactivating species. This effect was still more pronounced when increasing the initial monomer-to-initiator molar ratio from 50 to 200.[11]

The present communication aims at reporting on the synthesis of poly[(ethylene oxide)-*block*- (sodium 2-acrylamido-2-methyl-1-propane sulfonate)] diblock copolymers [P($EO_m$-*b*-$AMPS_n$)] with predictable number-average molar masses and narrow polydispersities by water-based ATRP. To the best of our knowledge, the preparation of such well-defined block copolymers has not been reported yet, as the introduction of chelating PEO segments towards a copper catalyst is an additional parameter to be taken into account in setting up the water-based ATRP of AMPS.[9] As 2,2′-bipyridyl (Bpy) was demonstrated to be a good ligand for water-based copper-mediated ATRP,[12,13] the polymerization has been carried out using α-methoxy-ω-(2-methylbromoisobutyrate) poly(ethylene oxide)s (MeO-P[EO]$_m$-Br$^i$B) with *m* ranging from 12 to 113 and CuBr · 2Bpy as the macroinitiator and catalyst, respectively, by modulating various parameters such as solvent composition, polymerization temperature, and addition of extra halide ions in the form of NaCl (Scheme 3).



Scheme 2. Schematic representation of the basic equilibria in water-based ATRP; RX—alkyl halide (X = Br or Cl); $k_{act}$, $k_{deact}$, and $k_{term}$ are the rate constants of activation, deactivation, and termination stage, respectively.

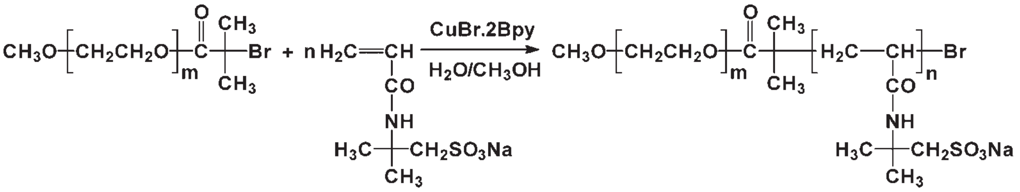
## Experimental Part

### *Materials*

Sodium 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS, acidic form, 99%, $\overline{M}_w = 207.25$ g · mol$^{-1}$, Aldrich), 2-bromo-2-methylpropionylbromide (Br$^i$BBr, 98%, $\overline{M}_w = 229.90$ g · mol$^{-1}$, $d = 1.86$, Aldrich), α-methoxy-ω-hydroxy poly(ethylene oxide) oligomers (MeO-P[EO]$_m$-OH; $m = 12$ ($\overline{M}_n = 550$ g · mol$^{-1}$, $\overline{M}_w/\overline{M}_n = 1.06$, Aldrich), $m = 45$ ($\overline{M}_n = 2\,000$ g · mol$^{-1}$, $\overline{M}_w/\overline{M}_n = 1.06$, Fluka) and $m = 113$ ($\overline{M}_n = 5\,000$ g · mol$^{-1}$, $\overline{M}_w/\overline{M}_n = 1.06$, Fluka)), 2,2′-bipyridyl (Bpy, >99%, $\overline{M}_w = 156.18$ g · mol$^{-1}$, Aldrich) and copper (I) bromide (CuBr, >99%, $\overline{M}_w = 143.45$ g · mol$^{-1}$, Aldrich) were used as received. Triethylamine (99%, $\overline{M}_w = 101.19$ g · mol$^{-1}$, $d = 0.726$ g · mol$^{-1}$, Fluka) was dried over barium oxide for 48 h and distilled just before use. Tetrahydrofuran (THF, Labscan, 99%) was dried by refluxing over Na/benzophenone complex, and distilled just before use. All other reagents were of analytical grade, and used as received.

### *Synthesis and Characterization of α-Methoxy-ω-(2-bromo-2-methylisobutyrate) Poly(ethylene oxide)s (MeO-P[EO]$_m$-Br$^i$B with $m = 12$, 45, and 113)*

In a typical experiment, MeO-P[EO]$_{12}$-OH (30 g, 54 mmol) and triethylamine (11.4 mL, 81 mmol) were dissolved in 50 mL THF and added dropwise with a solution of Br$^i$BBr (10.1 mL, 81 mmol) in 30 mL THF. After 24-hour stirring at room temperature (r.t.), precipitated ammonium salts were filtrated out and charcoal was added to the supernatant to adsorb Br$^i$BBr in excess. After a second filtration, MeO-P[EO]$_{12}$-Br$^i$B was



Scheme 3. Sketch of P(EO$_m$-*b*-AMPS$_n$) diblock copolymers synthesis by copper-mediated ATRP in a water/methanol mixture.

dried at 60 °C under reduced pressure up to constant weight. Completion of the esterification reaction was attested by $^1$H NMR spectroscopy from the relative intensity of the methylene protons of ethylene oxide repetitive units at 3.65 ppm and the methyl protons of isobutyrate end-groups at 1.89 ppm. Recovery yield reached 80%. $^1$H NMR (300 MHz, CDCl$_3$, ppm): $\delta = 1.89$ (Br-C(C$\underline{H}_3$)$_2$–CO), 3.34 (C$\underline{H}_3$O–(CH$_2$–CH$_2$–O)$_m$), 3.65 (CH$_3$O–(C$\underline{H}_2$–C$\underline{H}_2$–O)$_{m\text{-}1}$–C$\underline{H}_2$–CH$_2$–O–CO), 4.25 (CH$_3$O–(CH$_2$–CH$_2$–O)$_{m\text{-}1}$–CH$_2$–C$\underline{H}_2$–O–CO).

### *Synthesis and Characterization of P(EO$_m$-b-AMPS$_n$) Block Copolymers*

The polymerization was performed in distilled water or water/methanol mixtures (1:1 or 3:1, v/v) using MeO-P[EO]$_m$-Br$^i$B as macroinitiators and CuBr · 2Bpy as catalyst. For sample 7 in Table 1, a dry flask was charged with CuBr (0.05 g, 0.35 mmol), Bpy (0.11 g, 0.7 mmol) and a magnetic stirrer. The flask was fitted with a rubber septum and degassed with three successive vacuum–nitrogen cycles. A second flask was charged with MeO-P[EO]$_{12}$-Br$^i$B (0.24 g, 0.35 mmol), methanol (5 mL), NaCl (0.04 g, 0.7 mmol) and a solution of AMPS (15 mL) as obtained by previous titration of AMPS (5 g, 24.2 mmol) in distilled water by dropwise addition of NaOH solution until adjusting the pH at 10. The flask was fitted with a rubber septum and degassed under N$_2$ flow for a few minutes. This mixture was then transferred into the first flask and the polymerization was carried out under stirring at 60 °C for 3 h. The copolymer was recovered by precipitation in seven-fold excess of cold acetone, filtration and drying up to constant weight. Copper catalyst was removed by filtration of an aqueous copolymer solution through a silica gel column. Residual copper content was determined using Jobin Yvon 38-Plus inductively coupled plasma atomic emission spectrometer using the following protocol. Approximately 250 mg of polymer was accurately weighed, dissolved in distilled water containing 2% nitric acid and diluted to 50 mL. The unknown aqueous polymer solution was introduced into the argon plasma and the copper emission at 324.754 nm was measured and compared to that found for stock solutions 10, 5, 3, 1, 0.5, and 0.1 ppm Cu; a blank solution containing 2% nitric acid in distilled water was used as the seventh calibration solution. The manufacturer estimated detection limit is around 0.001 ppm for the above emission wavelength. P(EO$_m$-*b*-AMPS$_n$) copolymers were characterized by $^1$H NMR using a Bruker AMX-300 apparatus at r.t. in D$_2$O (see Figure 1). Molecular weight

Table 1. Effect of solvent composition, temperature, and extra halide addition (NaCl) on the monomer conversion and molecular weight parameters of P(EO$_{12}$-*b*-AMPS) diblock copolymers as initiated by MeO-PEO$_{12}$-Br$^i$B macroinitiator for 3 h and initial [AMPS]/[MeO-PEO$_{12}$-Br$^i$B]/[CuBr]/[Bpy] molar ratios of 70/1/1/2 ([AMPS]$_0 = 1.2$ mol · L$^{-1}$ and pH = 10).

| Entry | Solvent composition | $T$ | [NaCl]/[init] | Conv.a) | PolyAMPS block | | | Diblock copolymers |
|---|---|---|---|---|---|---|---|---|
| | v/v | °C | | % | $\bar{M}_{\text{ntheor}}$ b) | $\bar{M}_{\text{nexp}}$ c) | $f$ d) | $\bar{M}_w/\bar{M}_n$ e) |
| 1 | H$_2$O | r.t. | 0 | 78 | 12 600 | 37 300 | 0.34 | 3.08 |
| 2 | H$_2$O | 60 | 0 | 52 | 11 200 | 26 600 | 0.42 | 2.40 |
| 3 | H$_2$O | 80 | 0 | 79 | 12 800 | 79 700 | 0.16 | 3.46 |
| 4 | H$_2$O/MeOH (1:1) | r.t. | 0 | 84 | 13 700 | 16 700 | 0.82 | 2.15 |
| 5 | H$_2$O/MeOH (3:1) | r.t. | 0 | 60 | 9 600 | 11 400 | 0.84 | 1.40 |
| 6 | H$_2$O/MeOH (3:1) | r.t. | 2 | 41 | 6 600 | 10 300 | 0.64 | 1.39 |
| 7 | H$_2$O/MeOH (3:1) | 60 | 2 | 56 | 8 900 | 12 600 | 0.71 | 1.33 |

a) Conversion as determined after precipitation in cold acetone: Conv. = ($m$-$m_I$-$m_{Cu}$-$m_L$)/$m_M$ where $m$ denotes the weight of product, and $m_I$, $m_{Cu}$, $m_L$, and $m_M$ the weights of the initiator, copper catalyst, ligand (Byp), and monomer, respectively.

b) Theoretical number-average-molar mass as calculated by $\bar{M}_{\text{ntheor}} = [\text{AMPS}]/[\text{MeO-PEO}_{12}\text{-Br}^i\text{B}] \times \text{conv.} \times \bar{M}_w\text{AMPS}$ assuming a living process.

c) Experimental number-average molar mass as determined by $^1$H NMR spectroscopy (see Figure 1): $\bar{M}_{\text{nexp}} = \overline{DP}_{\text{exp}} \times \bar{M}_w\text{AMPS}$, where $\overline{DP}_{\text{exp}}$ is the experimental degree of polymerization, as calculated from the relative intensities of the methylene protons of PEO sequence (**g**, $\delta = 3.65$ ppm) and of the methylene protons of C$\underline{H}_2$-SO$_3$Na group of AMPS units (**b**, $\delta = 3.32$ ppm).

d) Efficacy as calculated from $\bar{M}_{\text{ntheor}}/\bar{M}_{\text{nexp}}$.

e) Polydispersity index as determined by SEC in 0.05 M CH$_3$COOH/CH$_3$COONa aqueous solution.

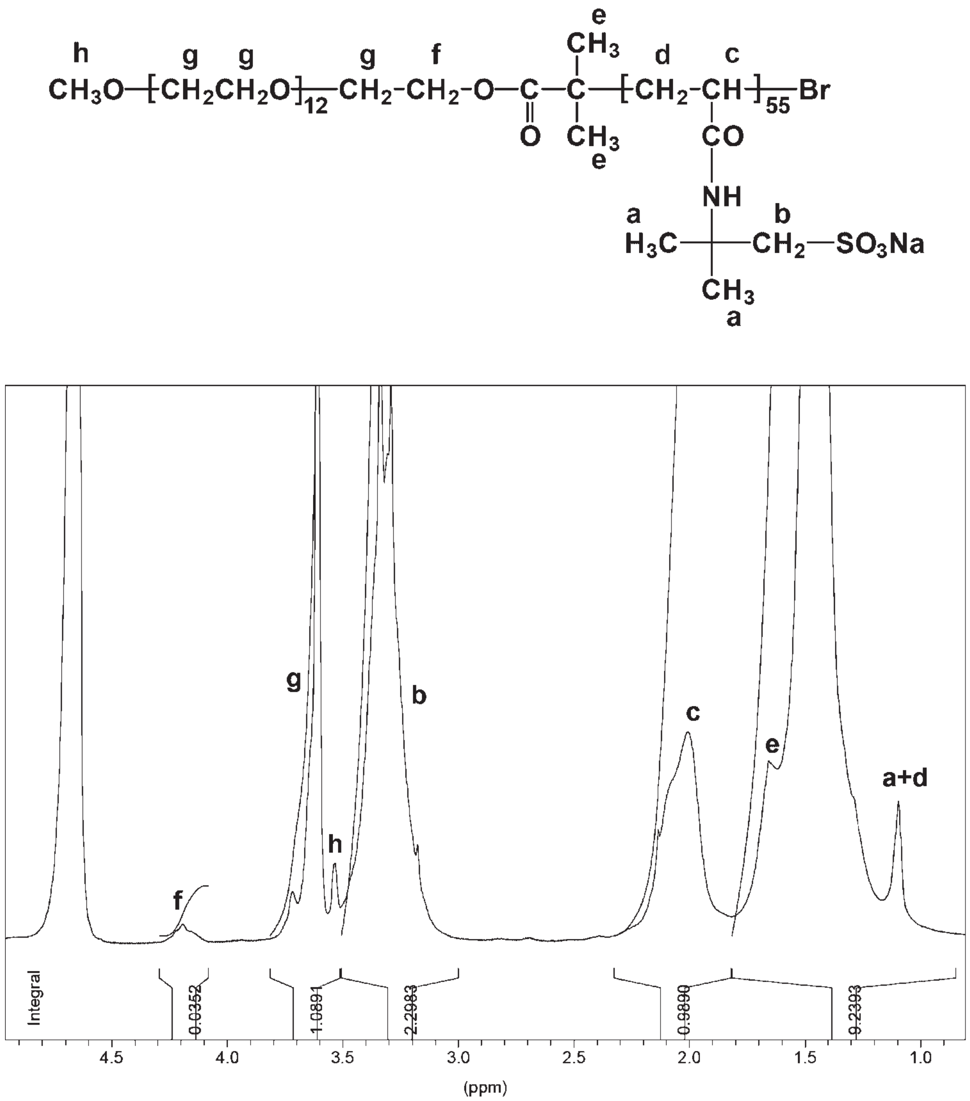


Figure 1. $^1$H NMR spectrum of P(EO$_{12}$-*b*-AMPS$_{55}$) diblock copolymer in $D_2O$ (entry 7, Table 1).

distribution of P(EO$_m$-*b*-AMPS$_n$) was determined by size exclusion chromatography (SEC) in 0.05 M $CH_3COOH$/$CH_3COONa$ aqueous solution at 30 °C using an Agilent 1100 Series liquid chromatograph (flow rate = 1 mL · min$^{-1}$, loop volume 100 μL, and solution concentration = 1 mg · mL$^{-1}$) equipped with two PL aquagel-OH mixed 8 μm columns. For calibration, poly(ethylene oxide)s standards ($\overline{M}_w$ = 600–50 000, Polymer Laboratories) were used.

## Results and Discussion

The synthesis of P(EO$_m$-*b*-AMPS$_n$) copolymers has been performed by ATRP of AMPS ([AMPS]$_0$ = 1.2 mol · L$^{-1}$) in distilled water or water/methanol mixtures for 3 h at various temperatures from r.t. up to 80 °C by using α-methyl-ω-2-bromoisobutyrate poly(ethylene oxide)s (MeO-P[EO]$_m$-Br$^i$B with $m$ = 12, 45, and 113) and CuBr ligated by 2,2′-bipyridyl (Bpy) as macroinitiators and catalyst, respectively. The initial [AMPS]/[MeO-P[EO]$_m$-Br$^i$B]/[CuBr]/[Bpy] molar ratio has been fixed at 70/1/1/2. Table 1 shows the effect of various parameters tuned out for controlling P(EO$_m$-*b*-AMPS$_n$) molecular weight parameters, i.e., number-average molar mass ($\overline{M}_n$) and polydispersity index ($\overline{M}_w/\overline{M}_n$).

In the first series of experiments (entries 1 to 3, Table 1), water has been used as the solvent while varying the polymerization temperature. In fact, it has been examined whether improved control might be achieved on the polymerization by increasing the temperature as a result of a significant increase of $k_{deact}$ over $k_{term}$ rate constants (Scheme 2).[13] It came out that ATRP remains fast in water mainly due to the dissociation of the deactivator and that the relative increase in $k_{deact}$ may not be large enough to make the higher temperature very suitable, except for 60 °C which

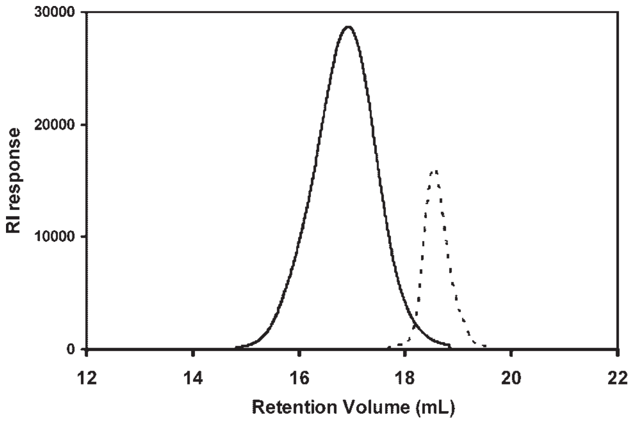


Figure 2. SEC of P($EO_{45}$-*b*-$AMPS_{60}$) diblock copolymer (entry 1, Table 2) and MeO-P[EO]$_{45}$-Br$^{i}$B macroinitiator (dashed line).

tends to induce a slightly higher efficacy parameter, $f = \overline{M}_{\text{ntheor}}/\overline{M}_{\text{nexp}}$, together with a lower polydispersity index ($f = 0.42$ and $\overline{M}_w/\overline{M}_n = 2.40$). It has been reported elsewhere that the rate of deactivation is directly correlated to the concentration of water in any aqueous water-based mixed solvent.[9] Therefore, increasing volumes of methanol have been added to water (entries 4 and 5, Table 1). In perfect agreement with the evolution of halogenophilicity of bromide-based deactivating complex in protic media,[9] the dissociation of $Cu^{II}Br_2 \cdot 2Bpy$ complex into $Cu^{II}.Bpy(H_20) +$ $Br(H_20)_j$ ($j = 1,\ldots,m$) becomes less pronounced for a water/methanol composition of 3:1 by volume. In such conditions, theoretical and experimental molecular weights are closer ($f = 0.84$) and the polydispersity index reaches 1.40, even at r.t. Then, the effect of adding sodium chloride (2:1 vs. the macroinitiator), i.e., extra halide ions, on the stability of the deactivator complex has been evaluated at r.t. or 60 °C (entries 6 and 7, Table 1). As might be expected for such a low amount of NaCl added, the beneficial effect is restricted. Figure 1 shows the $^1$H NMR spectrum of P($EO_{12}$-*b*-$AMPS_{55}$) diblock copolymer (entry 7, Table 1). The number-average molar mass ($\overline{M}_n$) of the polyAMPS block is calculated from the relative intensity of the methylene protons of ethylene oxide repetitive units (H**g** at 3.8 ppm) and the methylene sodium sulfonate protons (H**b** at 3.4 ppm), knowing $\overline{M}_n$ of the macroinitiator. Finally, Table 2 reports on the molecular characteristics of P($EO_m$-*b*-$AMPS_n$) diblock copolymers as obtained by water-based ATRP of AMPS initiated by MeO-P[EO]$_m$-Br$^{i}$B with $m = 45$ and 113, and catalyzed by $CuBr \cdot 2Bpy$ in water/$CH_3OH$ (3:1, v/v) at 60 °C for 3 h. These experimental conditions allow to obtain strong copper chelating diblock copolymers with an acceptable correlation between theoretical and experimental $\overline{M}_n$ and a polydispersity index close to 1.4 even at quite high AMPS conversion (conversion = 80% for entry 2, Table 2). Figure 2 clearly shows the shift to higher elution volumes of P($EO_{45}$-*b*-$AMPS_{60}$) diblock copolymers (entry 1, Table 2) compared to the trace initially recorded for the macroinitiator. The copper catalyst was removed by dissolving the crude polymer in distilled water and passing through silica gel column. The resulting solution was colorless. The solvent was removed by evaporation under reduced pressure. The performed ICP-AES analysis of purified copolymer has shown that the residual copper content was lower than 1.0 ppm.

## Conclusion

Optimal conditions for the preparation of well-defined P($EO_m$-*b*-$AMPS_n$) diblock copolymers by copper-mediated ATRP in aqueous solution have been found which circumvent side reactions related to the slow deactivation rate in protic media. Combining blood compatible PAMPS

Table 2. Effect of the macroinitiator polymerization degree MeO-PEO$_m$-Br$^{i}$B on the monomer conversion and molecular weight parameters of P($EO_m$-*b*-AMPS) diblock copolymers as obtained after 3 h for initial [AMPS]/[MeO-PEO$_m$-Br$^{i}$B]/[CuBr]/[Bpy]/[NaCl] molar ratios of 70/1/1/2/2 in water/methanol mixture (3:1) at 60 °C ($[AMPS]_0 = 1.2$ mol · L$^{-1}$ and pH = 10).

| Entry | $\overline{DP}_{\text{PEO}}$ | Conv.[a] | PolyAMPS block | | | Diblock copolymers |
|---|---|---|---|---|---|---|
| | | % | $\overline{M}_{\text{ntheor}}$[b] | $\overline{M}_{\text{nexp}}$[c] | $f$[d] | $\overline{M}_w/\overline{M}_n$[e] |
| 1 | 45 | 60 | 7 800 | 13 700 | 0.56 | 1.39 |
| 2 | 113 | 81 | 13 000 | 26 000 | 0.50 | 1.40 |

[a] Conversion as determined after precipitation in cold acetone: Conv. = $(m\text{-}m_I\text{-}m_{Cu}\text{-}m_L)/m_M$ where $m$ denotes the weight of product, and $m_I$, $m_{Cu}$, $m_L$, and $m_M$ the weights of the initiator, copper catalyst, ligand (Byp), and monomer, respectively.

[b] Theoretical number-average-molar mass as calculated by $\overline{M}_{\text{ntheor}} =$ [AMPS]/[MeO-PEO$_m$-Br$^{i}$B] × conv. × $\overline{M}_w$AMPS assuming a living process.

[c] Experimental number-average molar mass as determined by $^1$H NMR spectroscopy (see Figure 1): $\overline{M}_{\text{nexp}} = \overline{DP}_{\text{exp}} \times \overline{M}_w$AMPS, where $\overline{DP}_{\text{exp}}$ is the experimental degree of polymerization, as calculated from the relative intensities of the methylene protons of PEO sequence (**g**, $\delta = 3.65$ ppm) and of the methylene protons of $C\underline{H}_2$-$SO_3Na$ group of AMPS units (**b**, $\delta = 3.32$ ppm).

[d] Efficacy as calculated from $\overline{M}_{\text{ntheor}}/\overline{M}_{\text{nexp}}$.

[e] Polydispersity index as determined by SEC in 0.05 M $CH_3COOH/CH_3COONa$ aqueous solution.

polyelectrolytes and PEO segments into a diblock copolymer architecture is of prime interest for the preparation of stealthy nanoparticles by polyelectrolyte complex formation. This will be the main topic of a forthcoming publication.

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