Synthesis of cationic star polymers by simplified electrochemically mediated ATRP

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Abstract. Cyclodextrin-based cationic star polymers were synthesized using β -cyclodextrin (β -CD) core, and 2-(dimethylamino)ethyl methacrylate (DMAEMA) as hydrophilic arms. Star-shaped polymers were prepared *via* a simplified electrochemically mediated ATRP (*se*ATRP) under potentiostatic and galvanostatic conditions. The polymerization results showed molecular weight (MW) evolution close to theoretical values, and maintained narrow molecular weight distribution (MWD) of obtained stars. The rate of the polymerizations was controlled by applying more positive potential values thereby suppressing star-star coupling reactions. Successful chain extension of the ω -functional arms with a hydrophobic *n*-butyl acrylate (BA) formed star block copolymers and confirmed the living nature of the β -CD-PDMAEMA star polymers prepared by *se*ATRP. Novelty of this work is that the β -CD-PDMAEMA-*b*-PBA cationic star block copolymers were synthesized for the first time *via se*ATRP procedure, utilizing only 40 ppm of catalyst complex. The results from ^1H NMR spectral studies support the formation of cationic star (co)polymers.

Keywords: polymer synthesis, *se*ATRP, amphiphilic star copolymers

1. Introduction

Atom transfer radical polymerization (ATRP) is proven to be one of the most versatile reversible deactivation radical polymerization (RDRP) methods that enables the preparation of polymers with controlled molecular weights (MWs), narrow molecular weight distributions (M_w/M_n , MWDs), and targeted degrees of polymerization (DP) [1–13]. The advent of low amount catalyst ATRP system, such as simplified electrochemically mediated ATRP (*se*ATRP) [14] offers more environmentally friendly reaction conditions for the synthesis of polymers [15]. In *se*ATRP a desired amount of the catalyst complex ($\text{X-Cu}^{\text{II}}/\text{L}$) can be electrochemically reduced to ($\text{Cu}^{\text{I}}/\text{L}$) activators to start a controlled polymerization [16]. The reduced activator then spreads out into reaction mixture by vigorous stirring, and reacts with initiators (P-X) to

form radical species ($\text{P}^{\bullet}$) and is oxidized back to ($\text{X-Cu}^{\text{II}}/\text{L}$). Consequently, the radical species propagate to form polymeric chains by reacting with monomers (M), or are deactivated back to the dormant species ($\text{P}_n\text{-X}$) (Figure 1) [14, 15, 17, 18].

This method has been applied to hydrophobic (meth)acrylates [14, 15, 19–26], and hydrophilic (meth)acrylates and (meth)acrylamides [14, 16–18, 25, 27–31] for the synthesis of well-defined polymeric architec-

Figure 1. Mechanism of *se*ATRP [19]

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tures. Star-shaped cationic polymers, consisting of multiple arms linked to a central β -cyclodextrin (β -CD) core, have recently attracted much attention, because of their dense branched architecture with moderate flexibility, tunable properties like solubility, chemically crosslinked structure, temperature or pH sensitivity, which could be manipulated by the parameters such as the block composition, MW, and arm number [32–44].

Amphiphilic star copolymers composed of poly(2-dimethylaminoethyl methacrylate)-*block*-poly(*n*-butyl acrylate) (PDMAEMA-*b*-PBA) arms covalently linked to a β -CD core are especially interesting, because they can be used in biomedical applications, including drug delivery and tissue engineering. PDMAEMA is the most extensively studied pH-responsive polymer [45–50], because it is able to function as the pH-responsive component as it has a nitrogen moiety, which can be protonated by lowering the pH of the solution [48, 49], and shows pH-dependent lower critical solution temperature behavior [45] and upper critical solution temperature behavior at low temperatures in the presence of multivalent counter ions [47]. Furthermore PBA is an industrially important polymer because of its low glass-transition temperature, durability, and potential use as a soft segment in thermoplastic elastomers [51, 52].

The main objective of this article is to report the first example of the preparation of well-defined star-shaped cationic polymers, consisting of the β -CD core and the respective PDMAEMA and PDMAEMA-*b*-PBA arms by *se*ATRP, under both potentiostatic and galvanostatic conditions. In this case, the arm of the star polymer is composed of a cationic PDMAEMA block and a hydrophobic PBA block. It was presented that polymerization conditions were optimized (including the effect of applied potential on the polymerization behavior) to provide fast reactions while employing low catalyst concentrations and preparation of star copolymers with narrow MWDs. Therefore, well-defined cationic block star copolymers, with a β -CD core were successfully produced through appropriate selection of experimental conditions.

2. Experimental section

2.1. Materials

β -Cyclodextrin (β -CD, $M_n = 1,135$), 2-bromoisobutyl bromide (BriBBR, 98%), *N*-methyl-2-pyrroli-

done (NMP, >99%), dichloromethane (DCM, >99.5%), *n*-hexane (95%), sodium bicarbonate (>99.7%), tetrabutylammonium perchlorate (TBAP, >98%), copper(II) bromide ($\text{Cu}^{\text{II}}\text{Br}_2$, 99.999%), and methylated cellulose (Tylose, MH = 300) were purchased from Aldrich, USA. *N,N*-Dimethylformamide (DMF, 99.9%) was purchased from Acros, Belgium. These reagents were used without further purification. Tris(2-pyridylmethyl)amine (TPMA) was prepared according to a published procedure [53]. Stock solutions of $\text{Cu}^{\text{II}}\text{Br}_2$ and TPMA were prepared according to a previously described in reference [18]. The β -CD- Br_{21} ATRP initiator was prepared by reacting β -CD with BriBBR in NMP according to procedure described in reference [54] and characterized according to our previous work [15]. 2-(Dimethylamino)ethyl methacrylate (DMAEMA; 98%; Sigma-Aldrich, USA) and *n*-butyl acrylate (BA; >99%; Sigma-Aldrich, USA) were passed through a column filled with basic alumina prior to use to remove any inhibitor. Platinum (Pt) wire, Pt gauge mesh and Pt disk (3 mm diameter, Gamry) were purchased from Alfa Aesar, USA. All cyclic voltammetry (CVs) and preparative electrolysis were conducted in electrochemical cell kit (Gamry, USA).

2.2. Analysis

^1H NMR spectra in CDCl_3 were measured using Bruker Avance 500 MHz spectrometer. Monomer conversion and theoretical number-average molecular weight ($M_{n,\text{th}}$) were determined by NMR based on the previous research [17]. MWs and MWDs were determined by GPC (Polymer Standards Services (PSS) columns (guard, 10^5 , 10^3 , and 10^2 Å), with THF eluent, flow rate 1.00 mL/min, and with a differential refractive index (RI) detector (Viscotek, T60A)). The apparent molecular weights (MWs) and dispersity (M_w/M_n) were determined with a calibration based on PS standards using TRISEC software. CVs and preparative electrolysis were recorded on a Metrohm Autolab potentiostat (AUT84337) using GPES software from EcoChemie B. V. Corporation. The electrolysis were carried out under Ar atmosphere using a Pt disk for CV, ($A = 0.071 \text{ cm}^2$) and Pt mesh for preparative electrolysis, ($A = \sim 6 \text{ cm}^2$) working electrodes (WE). The counter electrode (CE, sacrificial anode) was Al wire ($l = 10 \text{ cm}$, $d = 1 \text{ mm}$). Values for potentials applied for preparative electrolysis were

established from CV measurements at a 100 mV/s scan rate using saturated calomel electrode (SCE; Gamry) reference electrode (RE) according to the previous research [15].

2.3. Synthesis of β -CD-(PDMAEMA)₂₁ star polymers by *se*ATRP

The synthesis of β -CD-(PDMAEMA)₂₁ star polymers was conducted under potentiostatic and galvanostatic conditions (Figure 2).

TBAP (1.64 g, 5 mmol) was placed in an electrolysis cell maintained at 50 °C under an Ar purge. Then, 12 mL of Ar purged DMAEMA (71 mmol), DMF (8.9 mL) and 57 μ L of Cu^{II}Br₂/2TPMA stock solution (0.05 M in DMF) were added to the reaction cell. The CV was recorded using a Pt disk WE, a SCE RE, and an Al wire CE for determining the appropriate applied potential ($E_{app} = E_{pc}$, $E_{app} = E_{pc}-30$ mV, $E_{app} = E_{pc}-60$ mV, and $E_{app} = E_{pc}-100$ mV). A solution of 451 mg of β -CD-Br₂₁ (0.11 mmol) in 3 mL of DMF was injected to the reaction solution and the CV was measured to confirm an increased cathodic response. Then the Pt mesh WE, Al wire CE, and SCE RE were prepared and immersed in the polymerization solution and the selected potential was applied using the preparative electrolysis method.

After the initial *se*ATRP polymerization under potentiostatic conditions the proper applied current values were calculated based on $I = Q/s$ for each step. An identical reaction mixture was prepared and the polymerization was carried out under multiple applied currents ($I_{app,1} = (-) 0.52$ mA (0.33 h), $I_{app,2} = (-) 0.30$ mA (0.33 h), $I_{app,3} = (-) 0.19$ mA (0.56 h), $I_{app,4} = (-) 0.09$ mA (0.56 h), $I_{app,5} = (-) 0.04$ mA

(1.22 h)). In both cases samples were withdrawn periodically to follow the monomer conversion, using ¹H NMR. The M_n and M_w/M_n were determined by GPC measurements (with PS standard curve). The product was purified by dialysis against water (Spectra/Por dialysis membrane, MWCO 1000, Spectrum Laboratories Inc.), dried by air, dissolved in acetone, passed through a neutral alumina column in order to remove catalyst, and dried under vacuum for 5 days. The polymer was then isolated and characterized using ¹H NMR.

2.4. Chain extension of a β -CD-(PDMAEMA)₂₁ star macroinitiator with BA

The synthesis of β -CD-(PDMAEMA-*b*-PBA)₂₁ star block copolymers was conducted under potentiostatic and galvanostatic conditions (Figure 3).

The *se*ATRP method was also used for the chain extension of the β -CD-(PDMAEMA-Br)₂₁ macroinitiator with BA. Polymerization conditions: $[BA]_0/[\beta\text{-CD-(PDMAEMA-Br)}_{21}]_0/[Cu^{II}Br_2/2TPMA]_0 = 32/1/0.0013$, $[BA]_0 = 2.1$ M in DMF, $[Cu^{II}Br_2/2TPMA]_0 = 0.08$ mM, $[TBAP]_0 = 0.2$ M, $E_{app} = E_{pc}-60$ mV (vs. SCE), $T = 50$ °C, WE = Pt mesh, CE = Al wire, and RE = SCE. An identical reaction mixture was prepared and *se*ATRP was carried out under multiple applied currents ($I_{app,1} = (-) 0.38$ mA (0.67 h), $I_{app,2} = (-) 0.15$ mA (0.67 h), $I_{app,3} = (-) 0.04$ mA (0.67 h), $I_{app,4} = (-) 0.01$ mA (1.0 h)). In both cases samples were withdrawn periodically to follow the monomer conversion, using ¹H NMR. The M_n and M_w/M_n were determined by GPC measurements (with PS standard curve). The product was purified by dialysis against water and methanol (MWCO 1000), and

Figure 2. Synthesis of β -CD-(PDMAEMA)₂₁ star polymers via *se*ATRP

Figure 3. Synthesis of β -CD-(PDMAEMA-*b*-PBA)₂₁ star block copolymers via seATRP

dried under vacuum for 5 days. The polymer was then isolated and characterized using ^1H NMR.

3. Results and discussion

Well-controlled ATRP synthesis of star polymers is challenging when chain extension occurs from a macroinitiator of lower activity to a more active monomer [24]. The rate of activation of a bromo-terminated PDMAEMA chain end is faster than the ac-

tivation of a 2-bromoisobutyrate β -CD chain ends (ω -functional arms) [55, 56]. Typically, halogen exchange procedures [55–58] are employed to solve this problem, but it can't be used for systems with low concentrations of catalyst, because of poor initiation efficiency.

Here we have demonstrated new proposition of solving the problem with poor initiation efficiency by seATRP procedure. In this paper synthesis of cation-

Table 1. Summary of cationic star polymers synthesis by seATRP

Entry	$[\text{M}]_0/[\text{I}]_0/[\text{Cu}^{\text{II}}\text{Br}_2/2\text{TPMA}]_0$	$E_{\text{app}}^{(\text{a})}$	$k_p^{\text{app}(\text{b})}$ [h^{-1}]	Conv ^(b) [%]	DP _{app} ^(b) (per arm)	$M_{\text{n,theo}}^{(\text{c})}$ ($\cdot 10^{-3}$)	$M_{\text{n}}^{\text{app}(\text{d})}$ ($\cdot 10^{-3}$)	$M_{\text{w}}/M_{\text{n}}^{(\text{d})}$
1	32/1/0.0013	E_{pc}	0.202	45	14	51.5	45.0	1.08
2	32/1/0.0013	$E_{\text{pc}}-30$ mV	0.417	70	23	78.7	67.7	1.09
3	32/1/0.0013	$E_{\text{pc}}-60$ mV	0.772	90	29	99.3	80.7	1.09
4	32/1/0.0013	$E_{\text{pc}}-100$ mV	0.947	94	30	103.9	135.0	1.63
5	32/1/0.0013	Galvanostatic conditions ^(e)	0.709	88	28	97.1	78.5	1.08
6	32/1/0.0013	$E_{\text{pc}}-60$ mV	0.577	82	26	167.7	135.6	1.15
7	32/1/0.0013	Galvanostatic conditions ^(f)	0.523	79	25	165.1	132.0	1.14

General reaction conditions: $T = 50^\circ\text{C}$; $V_{\text{tot}} = 24$ mL (except entry 6 and 7: $V_{\text{tot}} = 16$ mL); $t = 3$ h; $[\text{M}]_0$: $[\text{DMAEMA}]_0 = 3.0$ M (except entry 6 and 7: $[\text{BA}]_0 = 2.1$ M); $[\text{I}]_0$: $[\beta\text{-CD-Br}_{21}]_0 = 4.4$ mM calculated per 21 Br (except entry 6 and 7: $[\beta\text{-CD-(PDMAEMA-Br)}_{21}]_0 = 3.1$ mM calculated per 21 Br); $[\text{Cu}^{\text{II}}\text{Br}_2/2\text{TPMA}]_0 = 0.12$ mM except entry 6 and 7: $= 0.08$ mM); $[\text{TBAP}]_0 = 0.2$ M. seATRP under potentiostatic conditions (WE = Pt mesh, CE = Al wire ($l = 10$ cm, $d = 1$ mm), RE = SCE): entries 1–4 and 6; seATRP under galvanostatic conditions (WE and CE without RE): entry 5 and 7.

^a E_{app} were selected based on CV analysis ($v = 100$ mV/s); ^bMonomer conversion, apparent propagation constants (k_p^{app}), and apparent practical degree of polymerization of monomer unit per arm (DP_{app}) were determined by NMR; ^c $M_{\text{n,theo}} = ([\text{M}]_0/[\text{MI}]_0) \times \text{conversion} \times M_{\text{monomer}} + M_{\text{initiator}}$; ^dapparent M_{n} and MWD were determined by THF GPC with PS standard; ^e $I_{\text{app}} = -0.52, -0.30, -0.19, -0.09$, and -0.04 mA for each steps; ^f $I_{\text{app}} = -0.51, -0.22, -0.11, -0.05$, and -0.03 mA for each steps.

ic star copolymers by *se*ATRP are reported for the first time using only 40 ppm of $\text{Cu}^{\text{II}}/\text{L}$ in solution. Table 1 summarizes the results of the star polymers synthesis using the β -CD based macroinitiator ($M_n = 4260$, $M_w/M_n = 1.06$) under both potentiostatic and galvanostatic conditions.

The structure of the ligand, monomer, dormant species as well as reaction conditions (solvent, temperature and pressure) can strongly influence the values of the rate constants (k_a , k_{da} and $K_{\text{ATRP}} (= k_a/k_{da})$) [5, 19]. In most cases electrochemically mediated ATRP reactions were carried out in DMF [14, 15, 19, 23, 24] and acetonitrile (MeCN) [20] as solvents. The polymerization in DMF was faster in comparison to the reactions conducted in MeCN, this is because more polar system could enhance ATRP equilibrium constants ($K_{\text{ATRP}} = k_a/k_{da}$) [59]. For example, K_{ATRP} value in aqueous condition is *ca.* 10^3 times higher than

MeCN condition. In contrast, less polar solvent condition such as anisole mixture would require higher concentration of the supporting electrolyte to achieve better conductivity [60]. Moreover it is well known that temperature plays a vital role in controlled polymerization systems, because the activation rate constants increased with increasing temperature [61, 62]. Thus, the objective of this study was to investigate and optimize polymerization conditions for *se*ATRP of DMAEMA (in terms of R_p , controlled MWs and narrow MWDs).

3.1. Influence of different applied potential

The effect of applied potential ($E_{\text{app}} = E_{\text{pc}}$, $E_{\text{app}} = E_{\text{pc}} - 30$ mV, $E_{\text{app}} = E_{\text{pc}} - 60$ mV, and $E_{\text{app}} = E_{\text{pc}} - 100$ mV) on the polymerization behavior was investigated as reported in Table 1, entries 1–4, and Figure 4. In essence, the fastest k_p^{app} (thereby R_p) and

Figure 4. Synthesis of β -CD-PDMAEMA star-shaped polymers as a function of applied potential; (a) current profile versus time, (b) first-order kinetic plots, (c) M_n and M_w/M_n versus monomer conversion, and (d) GPC results of DMAEMA polymerization for different E_{app} values (final GPC traces for each reactions). Reaction conditions: $[\text{DMAEMA}]_0/[\beta\text{-CD-Br}_{21}(\text{per}-\text{Br})]_0/[\text{Cu}^{\text{II}}\text{Br}_2/2\text{TPMA}]_0 = 32/1/0.0013$, $[\text{DMAEMA}]_0 = 3.0$ M, $[\text{Cu}^{\text{II}}\text{Br}_2/2\text{TPMA}]_0 = 0.12$ mM, $T = 50^\circ\text{C}$, $[\text{TBAP}]_0 = 0.2$ M, $V_{\text{tot}} = 24$ mL, $E_{\text{app}} = E_{\text{pc}}$, $E_{\text{app}} = E_{\text{pc}} - 30$ mV, $E_{\text{app}} = E_{\text{pc}} - 60$ mV, $E_{\text{app}} = E_{\text{pc}} - 100$ mV (vs. SCE).

larger cathodic currents (faster rate of reduction) were observed when more negative potential was applied (compare k_p^{app} ; Table 1, entries 4 vs. 1–3). In this case, faster rates of reduction provide a higher $[Cu^I/L]$ and $[P^*]$ leads to a higher R_p [19].

The polymerization results for more positive applied potentials (E_{pc} , $E_{pc}-30$ mV and $E_{pc}-60$ mV) showed a linear increase of M_n with conversion (Figure 4c), and low M_w/M_n values of obtained stars (Figure 4c–4d). On the other hand GPC trace of β -CD-PDMAEMA received at the most negative E_{app} ($E_{pc}-100$ mV, Figure 4d) showed the presence of a significant high molecular weight shoulder attributed to a higher occurrence of star-star intermolecular X-linking reaction *via* a coupling process as well as intramolecular coupling, which lead to less uniform growth of arms [63].

3.2. Synthesis of 21-arm star block copolymers

The preparation of CD star homopolymers with 21-arms of PDMAEMA under potentiostatic and galvanostatic conditions were carried out and the results are reported in Table 1, entries 3 and 5, Figure 5 and 6. Nearly identical first-order kinetic plots were observed (Figure 5b), with linear MW evolution (Figure 5c), and GPC analysis indicated narrow MWD (Figure 5a, 6a and 6b).

Chain end functionality was evaluated by chain extension from β -CD-(PDMAEMA₂₈)₂₁ macroinitiator ($M_n = 97\,100$, $M_w/M_n = 1.08$; Table 1, entry 5) with BA as the second monomer to form a star block copolymers under both copolymers under potentiostatic and galvanostatic conditions (Table 1, entries 6–7, Figure 7 and 8).

Figure 5. Multi-step preparative electrolysis for *seATRP*; (a) preparative electrolysis results from applied potential conditions (grey line) and applied current (black line), (b) first-order kinetic plot of monomer conversion versus time, and (c) M_n and M_w/M_n versus monomer conversion by potentiostatic and galvanostatic conditions. Reaction conditions: $[DMAEMA]_0/[\beta\text{-CD-Br}_{21} \text{ (per -Br)}]_0/[Cu^{II}Br_2/2TPMA]_0 = 32/1/0.0013$, $[DMAEMA]_0 = 3.0$ M, $[Cu^{II}Br_2/2TPMA]_0 = 0.12$ mM, $T = 50$ °C, $[TBAP]_0 = 0.2$ M, $V_{tot} = 24$ mL.

Figure 6. GPC traces of DMAEMA polymerization in the presence of β -CD-Br₂₁ under potentiostatic *se*ATRP (a) and galvanostatic *se*ATRP (b)

Figure 7. Multi-step preparative electrolysis for *se*ATRP; (a) preparative electrolysis results from applied potential conditions (grey line) and applied current (black line), (b) first-order kinetic plot of monomer conversion versus time, and (c) M_n and M_w/M_n versus monomer conversion by potentiostatic and galvanostatic conditions. Reaction conditions: $[BA]_0/[\beta\text{-CD-(PDMAEMA-Br)}_{21} \text{ (per -Br)}]_0/[\text{Cu}^{\text{II}}\text{Br}_2/2\text{TPMA}]_0 = 32/1/0.0013$, $[BA]_0 = 2.1 \text{ M}$, $[\text{Cu}^{\text{II}}\text{Br}_2/2\text{TPMA}]_0 = 0.08 \text{ mM}$, $T = 50^\circ\text{C}$, $[\text{TBAP}]_0 = 0.2 \text{ M}$, $V_{\text{tot}} = 16 \text{ mL}$.

Close to identical first-order kinetic plots were observed (Figure 7b), and DP of resulting copolymers increased linearly with monomer conversion (Figure 7c) indicating high initiation efficiency. The differences between theoretical and measured MW originate the differences in hydrodynamic radius of star

and linear polymer standards for GPC. Moreover, GPC analysis indicated narrow MWD (Figure 7c and 8a–b) confirming that the halogen end groups were preserved during the *se*ATRP of BA. In this case the % of chains terminated by radical means are below 1%, what indicating that *se*ATRP was conducted

Figure 8. GPC traces of BA polymerization in the presence of β -CD-(PDMAEMA-Br)₂₁ under different conditions: potentiostatic *se*ATRP (a) and galvanostatic *se*ATRP (b)

with preserved chain end functionality, therefore the bimodality cannot be detected by GPC, even if termination will be 100% of coupling. Probability of the intramolecular termination of acrylates can be enhanced due to a close proximity of radicals but also can be diminished due to radical segregation [15, 64].

3.3. Chemical structure of the 21-arm star polymers

The chemical structure of the synthesized β -CD-(PDMAEMA₂₈)₂₁ star polymer (Table 1, entry 5) and β -CD-(PDMAEMA₂₈-PBA₂₅)₂₁ star block copolymer (Table 1, entry 7) were confirmed by ¹H NMR spectroscopy (Figure 9 and 10).

The ¹H NMR spectrum shown in Figure 9 confirms the structure of β -CD-(PDMAEMA₂₈)₂₁ star cationic polymer obtained through *se*ATRP under galvanostatic conditions (Table 1, entry 5). The chemical shifts, 0.75–1.17, 1.72–2.09, 2.20–2.50, 2.51–2.86, and 3.78–4.34 ppm, are mainly attributable to the $-\text{CH}_3$ (α), $-\text{CH}_2-$ (β), $-\text{CH}_3$ (g), $-\text{CH}_2-$ (f), and $-\text{OCH}_2-$ (e) groups of the PDMAEMA units in the arms, respectively, indicating the presence of PDMAEMA chains [65]. While, in the ¹H NMR spectrum of the star block copolymer (Figure 10), the chemical shifts, 0.75–1.18m, 1.31–2.02, 2.18–2.55, 2.57–2.86, and 3.78–4.34 ppm, are mainly attributed by the $-\text{CH}_3$ (d), $-\text{CH}_2-$ ($\beta'+b+c$), $-\text{CH}-$ (α'), and $-\text{OCH}_2-$ (a) groups of the PBA units in the

Figure 9. ¹H NMR spectrum of CD star homopolymers with PDMAEMA arms (β -CD-(PDMAEMA₂₈)₂₁; Table 1, entry 5; $M_n = 97\,100$, $D = 1.08$) after purification (in CDCl_3)

Figure 10. ^1H NMR spectrum of star block copolymer $(\beta\text{-CD}-(\text{PDMAEMA}_{28}\text{-PBA}_{25})_{21})$; Table 1, entry 7; $M_n = 165\,100$, $D = 1.14$ after purification (in CDCl_3)

arms, respectively, indicating the presence of PBA chains [15].

4. Conclusions

The controlled 21-arm star polymers consisting of a β -CD core and PDMAEMA arms were successfully prepared *via* simplified electrochemically mediated atom transfer radical polymerization with low concentrations of catalyst (40 ppm of Cu^{II} species). The rate of the polymerizations was controlled by applying less negative E_{app} and therefore eliminating intermolecular termination reactions between growing arms. Chain extension of the initially formed hydrophilic star polymer with a more hydrophobic monomer (BA), confirmed the preservation of terminal halogen end group during the *se*ATRP of methacrylates. The use of a galvanostatic technique provided similar results to polymerizations conducted under potentiostatic conditions, providing polymers with molecular weight evolution close to theoretical values, while generating stars with narrow molecular weight distribution. Furthermore, the results from ^1H NMR spectral studies support the formation of star block (co)polymers. These new amphiphilic polyelectrolyte star copolymers are promising candidates for potential applications in biomedical fields, such as drug delivery, gene delivery, and antifouling coatings.

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