TBAP (1.37 g, 4 mmol) was placed in an electrolysis cell (50 °C, Ar). Then, 10 cm^3 of OEGA (23 mmol), 8 cm^3 of DMF (103 mmol), and 18 mm^3 of Cu^{II}Br$_2$/TPMA solution in DMF (0.05 dm^3) were added to the reaction cell. The CV was recorded using a Pt disk working electrode, a saturated calomel electrode (SCE) as a reference electrode, and an Al counter electrode for determining the applied potential ($E_{app} = E_{pc}$ - 85 mV). Next, a solution of 75 mg of GL-Br$_5$ (0.08 mmol) in 2 cm^3 of DMF was injected and the CV measurement was started. Then, the Pt mesh working electrode, Al counter and SCE reference electrodes were immersed in the reaction solution and the selected potential was applied using the controlled potential preparative electrolysis method. An identical reaction composition was prepared for the polymerization under multiple applied currents: $I_{app,1}$ = -0.20 mA (0.05 h), $I_{app,2}$ = -0.09 mA (0.15 h), $I_{app,3}$ = -0.05 mA (0.21 h), $I_{app,4}$ = -0.04 mA (0.97 h), $I_{app,5}$ = -0.03 mA (0.97 h), $I_{app,6}$ = -0.03 mA (0.97 h), $I_{app,7}$ = -0.02 mA (0.67 h). In both cases, samples were withdrawn periodically to follow the monomer conversion by ^{1}H NMR. The $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ were determined by GPC measurements (PS standards). The product was purified by dialysis against water and methanol (MWCO 1000), and dried under vacuum for 14 days. The polymer was then isolated and characterized using ^{1}H NMR. The arms of star polymers were cleaved by acid solvolysis according to [35]. The resulting polymer was characterized by GPC.

RESULTS AND DISCUSSION

A star polymer with a glucose-based core and hydrophilic OEGA arms was synthesized for the first time, using only 40 ppm of Cu catalyst, following the improved *se*ATRP procedure (Table 1). The reaction conditions were as follows: T = 50 °C; t = 4 h; total volume of reaction mixture V_{tot} = 20 cm^3; SW = ~ 6.3 cm^2 (entry 1), ~ 3.6 cm^2 (entry 2) or ~ 1.2 cm^2 (entries 3–4); molar ratios of reagents: [M]$_0$/[MI calculated per Br]$_0$/[Cu^{II}/L]$_0$/[E]$_0$ = 55/1/0.0022/9.7 where [M]$_0$ = [OEGA]$_0$ = 1.1 mol/dm^3; [MI] = [GL-Br$_5$]$_0$ = 4.1 mmol/dm^3; [Cu^{II}/L] = [Cu^{II}Br$_2$/TPMA] = 0.05 mmol/dm^3; [E]$_0$ = [TBAP]$_0$ = 0.2 mol/dm^3; $E_{app} = E_{pc}$ - 85 mV selected based on CV, ν = 100 mV/s (except entry 4 – electrolysis controlled by I_{app} = -0.20, -0.09, -0.05, -0.04, -0.03, -0.03, and -0.02 mA for each steps). Up to now, glucose polymers were prepared by ATRP with high amounts of catalyst, at least 5000 ppm of catalyst complex [26]. Another important issue concerns the possibility of reducing the size of the Pt cathodes, without significantly affecting the reaction rate, while offering a much easier and cheaper solution than replacing it with other, expensive, non-platinum electrodes such as Au [15, 16, 36, 37] or Fe [16].

Influence of the surface area of working electrodes to total volume of reaction mixture ratio

To investigate the possibility of reducing the cost of polymerization by changing the size of the Pt cathodes, without critically affecting the reaction rate, three separate experiments were conducted with various surface areas of the working electrodes; *i.e.*, SW = 6.3, 3.6, and 1.2 cm^2 corresponding to SW/V_{tot} = 0.31, 0.18, and 0.06 cm^{-1}, respectively entries 1—3 in Table 1 (Fig. 1–4).

The highest apparent propagation rate constant (k_p^{app}), thereby polymerization rate (R_p) and larger cathodic currents, *i.e.*, higher rate constant of reduction (k_{red}^{app}), which implies larger Cu^I/L regeneration rates (Table 1, Fig. 1b), were observed when higher SW/V_{tot} ratios were applied (Fig. 3). It was observed that as the SW/V_{tot} ratio increased, the R_p value increased with a square root dependence on the SW/V_{tot} ratio, in accordance with the equation [38–40]:

$$R_p = k_p[\mathrm{M}]\sqrt{\frac{[\text{X-Cu}^{\text{II}}/\text{L}]\left(\dfrac{SW}{V_{tot}}\right)\sqrt{\dfrac{D_o}{\pi}}}{k_t}} \tag{1}$$

where: k_p – propagation rate constant, D_o = 10.0 · 10^{-6} cm^2/s – value of the diffusion coefficient in the reduction of X-Cu^{II}/L to X-Cu^I/L, k_t – termination rate constant.

T a b l e 1. Summary of 5-arm star polymers synthesis by *se*ATRP

Entry	SW/V_{tot} cm^{-1}	k_p^{app} a) h^{-1}	k_{red}^{app} b) s^{-1}	$Conv$ a) %	GL-POEGA stars			POEGA arms					
					$\overline{M}_{n,th} \cdot 10^{-3}$ c)	$\overline{M}_{n,app} \cdot 10^{-3}$ d)	$\overline{M}_w/\overline{M}_n$ d)	$\overline{M}_{n,th} \cdot 10^{-3}$ e)	$DP_{n,th}$ f)	$\overline{M}_{n,app} \cdot 10^{-3}$ g)	$DP_{n,app}$ h)	$\overline{M}_w/\overline{M}_n$ g)	f_{IN} i), %
1	0.31	0.936	0.004	98	129.8	94.8	1.08	25.8	54	26.3	55	1.15	99
2	0.18	0.646	0.003	92	122.9	90.0	1.09	24.4	51	24.8	52	1.16	99
3	0.06	0.503	0.003	87	115.4	83.9	1.14	22.9	48	23.5	49	1.19	98
4	0.06	0.481	–	85	113.2	83.1	1.14	22.5	47	23.1	48	1.20	98

a) k_p^{app}, $Conv$ – apparent propagation constant and monomer conversion, respectively, both determined by NMR [12]; b) k_{red}^{app} – apparent reduction rate coefficient determined from first order plot of current *versus* time [40]; c) $\overline{M}_{n,th}$ = ([M]$_0$/[MI]$_0$) · $Conv$ · M_{M} + M_{MI} – theoretical $\overline{M}_n$ of 5-arm stars; d) $\overline{M}_{n,app}$, $(\overline{M}_w/\overline{M}_n)_{app}$ – apparent $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ of 5-arm stars, respectively, determined by GPC (THF eluent, PS standards); e) $\overline{M}_{n,th}$ = ($Conv$ · [M]$_0$)/[MI]$_0$ · M_{M} – theoretical $\overline{M}_n$ of the arms cleaved from the star polymers; f) $DP_{n,th}$ = ($Conv$ · [M]$_0$)/[MI]$_0$ – theoretical degree of polymerization per arm calculated from monomer to initiation site ratio and monomer conversion [42]; g) $\overline{M}_{n,app}$, $(\overline{M}_w/\overline{M}_n)_{app}$ – apparent $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ of the arms cleaved from the star polymers executed by GPC (THF eluent, PS standards); h) $DP_{n,app}$(arm) = $\overline{M}_{n,app}$(arm)/M_{M} – apparent degree of polymerization of one arm calculated from dividing $\overline{M}_{n,app}$ by the molar mass of the polymer's reiterating unit [41]; i) f_{IN} = [$DP_{n,th}$(arm)/$DP_{n,app}$(arm)] · 100 % – efficiency of initiation [45].