

Synthesis of high molecular weight five-arm star polymers by improved electrochemically mediated atom transfer radical polymerization

Paweł Chmielarz¹⁾

DOI: dx.doi.org/10.14314/polimery.2017.642

Abstract: Star-like polymers were designed with α -D-glucose (GL) as the core and oligo(ethylene glycol) acrylate (OEGA) for the arms *via* an improved type of simplified electrochemically mediated atom transfer radical polymerization (*se*ATRP) under preparative electrolysis conditions, utilizing only 40 ppm of the catalyst system. The novelty of this work is to present the possibility of reducing the size of the platinum cathode in the reaction setup without significantly affecting the polymerization rate under constant potential/current conditions. This is an easier and cheaper solution than replacing it with other, expensive, non-platinum electrodes such as Au or Fe. The results obtained from nuclear magnetic resonance (¹H NMR) and gel permeation chromatography (GPC) analyses clearly confirm the controlled nature of the electrochemically mediated polymerization of OEGA.

Keywords: polymer synthesis, glucose-based star polymers, simplified electrochemically mediated atom transfer polymerization, improved cathode.

Synteza pięcioramiennych polimerów gwiazdzistych o dużym ciężarze cząsteczkowym metodą ulepszonej kontrolowanej elektrochemicznie polimeryzacji rodnikowej z przeniesieniem atomu

Streszczenie: Stosując ulepszoną odmianę uproszczonej kontrolowanej elektrochemicznie polimeryzacji rodnikowej z przeniesieniem atomu (*se*ATRP) otrzymano polimery gwiazdziste z wykorzystaniem α -D-glukozy (GL) jako rdzenia i akrylanu oligooskyetylenu (OEGA) jako składowej ramion. Syntezę prowadzono w warunkach elektrolizy preparatywnej, z zastosowaniem bardzo małych stężeń katalizatora – na poziomie 40 ppm. Zbadano możliwości zmniejszenia rozmiaru katody platynowej w układzie reakcyjnym w stosunku do dotychczas używanych. Wykazano, że zmniejszenie to nie ma istotnego wpływu na szybkość polimeryzacji realizowanej w warunkach stałego potencjału/natężenia prądu. Zastosowane rozwiązanie jest łatwiejsze i tańsze niż stosowanie innych kosztownych katod nieplatynowych, takich jak Au lub Fe. Wyniki analiz wykonanych metodami magnetycznego rezonansu jądrowego (¹H NMR) i chromatografii żelowej (GPC) potwierdziły, że kontrolowana elektrochemicznie polimeryzacja OEGA przebiegała w sposób umożliwiający sterowanie tym procesem.

Słowa kluczowe: synteza polimerów, polimery gwiazdziste na bazie glukozy, uproszczona kontrolowana elektrochemicznie polimeryzacja rodnikowa z przeniesieniem atomu, ulepszona katoda.

The atom transfer radical polymerization (ATRP) technique is one of the most important methods applied in the synthesis of different types of polymers because of the optimization possibilities of the catalyst system [1–9]. Contrary to other ATRP methods, the simplified electrochemically mediated ATRP (*se*ATRP) [10] does not require the use of chemical compounds as reducing agents as they are replaced with an electrochemical control over the ratio

of the concentration of activator to deactivator by means of choosing an appropriate current level or potential that makes it possible to control the polymerization rate [10–14].

The typical *se*ATRP setup involves Pt/Al electrodes in an undivided cell, which makes it more affordable, attractive and, most of all, brings a beneficial energy saving in view of the minimization of the ohmic drop [10]. The application of this innovative setup, under both controlled potential and controlled current mode, has shown good results for *se*ATRP. The second solution is particularly attractive from an industrial and experimental standpoint because it eliminates the reference electrode compared with electrolysis under controlled potential conditions.

¹⁾ Rzeszów University of Technology, Faculty of Chemistry, Department of Physical Chemistry, Al. Powstańców Warszawy 6, 35-959 Rzeszów, Poland.

Author for correspondence; e-mail: p_chmiel@prz.edu.pl

Up to now, platinum [10–14] and other non-platinum electrodes (Fe and stainless steel) [15] have been the only materials used for the cathode in *se*ATRP. Other types of metallic electrodes cause several problems such as surface passivation, induction periods, and low conversions [16]. Platinum is an excellent electronic conductor and a chemically inert metal but it is expensive. Therefore, the aim of this work is to explore the possibility of reducing the size of the Pt cathode without significantly affecting the reaction rate under constant potential/current conditions.

Because of the wide interest in biocompatible, star-like polymers [17–23], the improved electrochemical polymerization of oligo(ethylene glycol) acrylate (OEGA) with an α -D-glucose core was investigated. Recently, α -D-glucose-based star-shaped polymers composed of poly[2-(dimethylamino)ethyl methacrylate] [24], poly[oligo(ethylene glycol) acrylate] [14], poly(*N*-isopropylacrylamide) [25], poly(*N*-vinyl pyrrolidone) [26], and poly(itaconic acid) [27] were synthesized using ATRP techniques. It is expected that these synthesized hydrophilic star polymers have great potential in tissue engineering and antifouling applications because of the biological compatibility of α -D-glucose (nutrient substance for metabolism in the human body) [25] and the characteristics of such polymers (non-toxic, non-immunogenic, antifouling and biocompatible) [28–32].

EXPERIMENTAL PART

Materials

α -D-Glucose (GL, $\overline{M}_n = 180.16$, 96 %), 2-bromoisobutyryl bromide (BriBBr, 98 %), pyridine (PY, 99.8 %), chloroform (CHCl_3 , > 99.8 %), tetrahydrofuran (THF, > 99.9 %), sodium bicarbonate (> 99.7 %), magnesium sulfate (MgSO_4 , > 99.5 %), methanol (MeOH, > 99.8 %), tetrabutylammonium perchlorate (TBAP, > 98 %), copper(II) bromide ($\text{Cu}^{\text{II}}\text{Br}_2$, 99.9 %), *n*-butanol (> 99.7 %), and sulfuric acid (> 95 %) were purchased from Aldrich. *N,N*-Dimethylformamide (DMF, 99.9 %) was purchased from Acros. Tris(2-pyridylmethyl)amine (TPMA) and $\text{Cu}^{\text{II}}\text{Br}_2$ solution were prepared according to reference [33]. The 1,2,3,4,6-penta-*O*-isobutyryl bromide- α -D-glucose (GL-Br₅) ATRP macroinitiator was prepared by reacting α -D-glucose with BriBBr in a solution of PY/ CHCl_3 according to the procedure described in references [14, 24]. Oligo(ethylene glycol) acrylate (OEGA, > 99 % from Aldrich) was passed through a column filled with basic alumina. Pt wire, Pt gauge mesh and Pt disks were purchased from Alfa Aesar, USA.

Experimental methods

Nuclear magnetic resonance ^1H NMR spectra obtained in CDCl_3 were used for the calculations of monomer conversion and theoretical, number-average molecular weights ($\overline{M}_{n,\text{th}}$) after measurement on a Bruker Avance 500 MHz spectrometer according to previously described research [34]. Number-average molecular weights (\overline{M}_n)

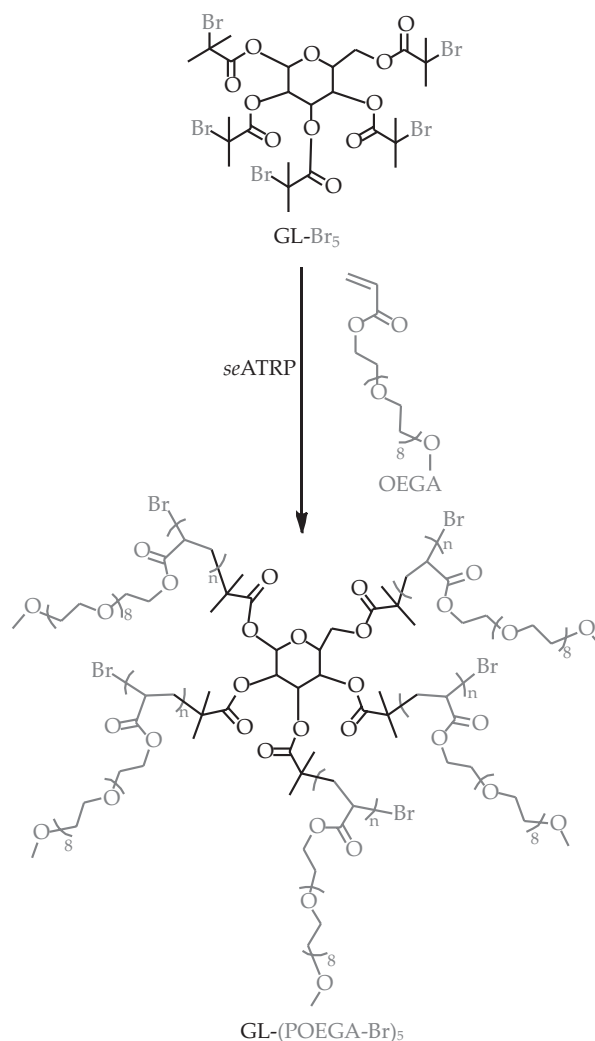
and molecular weight distributions, given by the $\overline{M}_w/\overline{M}_n$ ratio (where \overline{M}_w – weight-average molecular weight), were determined by gel permeation chromatography (GPC) with the following conditions: PSS columns (guard, 10^6 , 10^4 , and 10^3 nm), THF as eluent, Viscotek RI as detector, and calibration based on polystyrene (PS) standards.

Cyclic voltammetry (CV) and electrolysis were conducted in an electrochemical cell kit (Gamry, USA) and were recorded on a Metrohm Autolab potentiostat (AUT84337) using GPES EcoChemie software.

The preparative electrolyses were carried out under an Ar atmosphere using a Pt disk for CV, and Pt mesh for electrolysis (estimated geometrical surface area of the working electrodes were $SW = 6.3\text{--}1.2\text{ cm}^2$). The counter electrode was Al wire ($l = 10\text{ cm}$, $d = 1\text{ mm}$). Values for potentials applied for electrolysis were established according to previous research [11].

Synthesis of GL-(POEGA-Br)₅ star polymers via *se*ATRP

The synthesis of GL-(POEGA-Br)₅ star polymers was conducted by *se*ATRP under constant potential conditions according to Scheme A.



Scheme A

TBAP (1.37 g, 4 mmol) was placed in an electrolysis cell (50 °C, Ar). Then, 10 cm³ of OEGA (23 mmol), 8 cm³ of DMF (103 mmol), and 18 mm³ of Cu^{II}Br₂/TPMA solution in DMF (0.05 dm³) 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-Br₅ (0.08 mmol) in 2 cm³ 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 ¹H NMR. The \bar{M}_n and \bar{M}_w/\bar{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 ¹H 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 $V_{tot} = 20$ cm³; $SW = \sim 6.3$ cm² (entry 1), ~ 3.6 cm² (entry 2) or ~ 1.2 cm² (entries 3–4); molar ratios of reagents: $[M]_0/[MI]_0$ calculated per $Br_1/[Cu^{II}/L]_0/[E]_0 = 55/1/0.0022/9.7$ where $[M]_0 = [OEGA]_0 = 1.1$ mol/dm³; $[MI] = [GL-Br_5]_0 =$

4.1 mmol/dm³; $[Cu^{II}/L] = [Cu^{II}Br_2/TPMA] = 0.05$ mmol/dm³; $[E]_0 = [TBAP]_0 = 0.2$ mol/dm³; $E_{app} = E_{pc} - 85$ mV selected based on CV, $\nu = 100$ 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 cm² 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]:

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

where: k_p – propagation rate constant, $D_o = 10.0 \cdot 10^{-6}$ cm²/s – value of the diffusion coefficient in the reduction of X-Cu^{II}/L to X-Cu^I/L, k_t – termination rate constant.

Table 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					
					$\bar{M}_{n,th} \cdot 10^{-3}$ c)	$\bar{M}_{n,app} \cdot 10^{-3}$ d)	\bar{M}_w/\bar{M}_n d)	$\bar{M}_{n,th} \cdot 10^{-3}$ e)	$DP_{n,th}$ f)	$\bar{M}_{n,app} \cdot 10^{-3}$ g)	$DP_{n,app}$ h)	\bar{M}_w/\bar{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) $\bar{M}_{n,th} = ([M]_0/[MI]_0) \cdot Conv \cdot M_M + M_{MI}$ – theoretical \bar{M}_n of 5-arm stars; d) $\bar{M}_{n,app}$ (\bar{M}_w/\bar{M}_n)_{app} – apparent \bar{M}_n and \bar{M}_w/\bar{M}_n of 5-arm stars, respectively, determined by GPC (THF eluent, PS standards); e) $\bar{M}_{n,th} = (Conv \cdot [M]_0)/[MI]_0 \cdot M_M$ – theoretical \bar{M}_n of the arms cleaved from the star polymers; f) $DP_{n,th} = (Conv \cdot [M]_0)/[MI]_0$ – theoretical degree of polymerization per arm calculated from monomer to initiation site ratio and monomer conversion [42]; g) $\bar{M}_{n,app}$ (\bar{M}_w/\bar{M}_n)_{app} – apparent \bar{M}_n and \bar{M}_w/\bar{M}_n of the arms cleaved from the star polymers executed by GPC (THF eluent, PS standards); h) $DP_{n,app}(\text{arm}) = \bar{M}_{n,app}(\text{arm})/M_M$ – apparent degree of polymerization of one arm calculated from dividing $\bar{M}_{n,app}$ by the molar mass of the polymer's reiterating unit [41]; i) $f_{IN} = [DP_{n,th}(\text{arm})/DP_{n,app}(\text{arm})] \cdot 100$ % – efficiency of initiation [45].

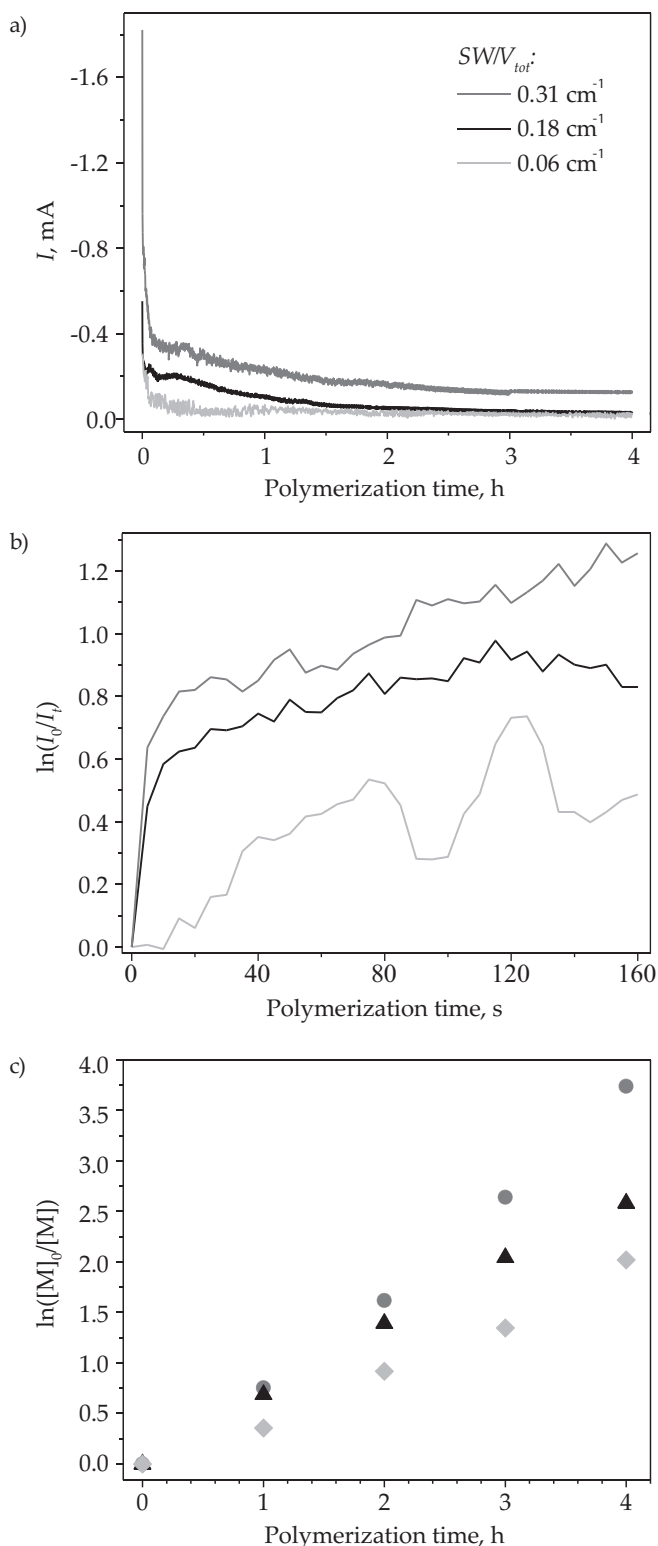


Fig. 1. Effect of SW/V_{tot} ratio on the synthesis of glucose-based star polymers shown as: a) current profile, b) first order plot of current, c) first order kinetic plot of monomer conversion

In this case R_p is defined as [39]:

$$R_p = k_p[M][P_n^*] = k_p[M] \sqrt{\frac{[X-Cu^{II}/L]k_{red}^{app}}{k_t}} \quad (2)$$

where: $[P_n^*]$ – concentration of propagating radicals.

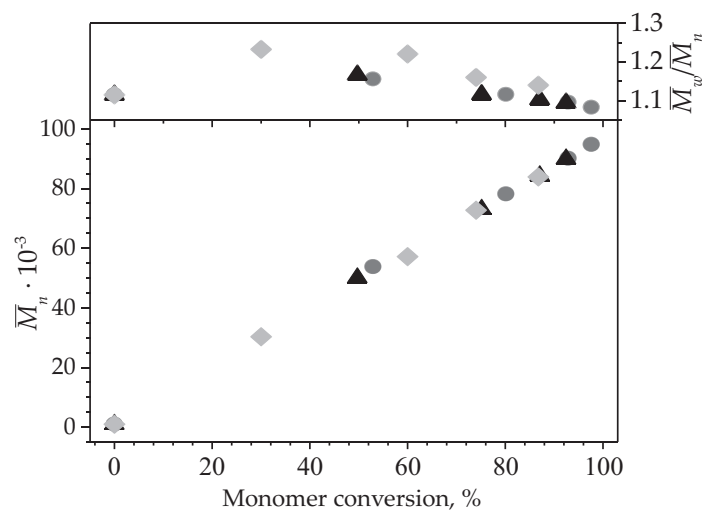


Fig. 2. Effect of SW/V_{tot} ratio on evolution of \bar{M}_n and \bar{M}_w/\bar{M}_n versus monomer conversion during the synthesis of glucose-based star polymers

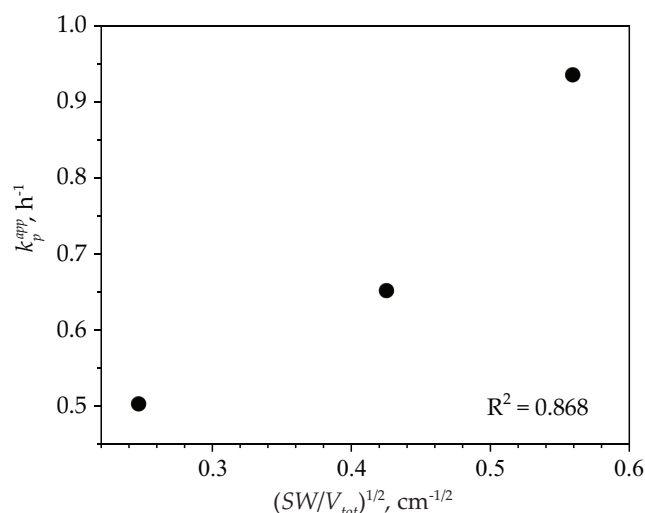


Fig. 3. Effect of SW/V_{tot} ratio on apparent polymerization rate coefficient (k_p^{app})

The reduction of deactivator rate constant can be presented as [38]:

$$k_{red}^{app} = \left(\frac{SW}{V_{tot}}\right) \sqrt{\frac{D_o}{\pi}} \quad (3)$$

The k_p^{app} is proportional to the root of the reduction rate constant $[k_{red}^{app} = \ln(I_0/I)]$ [40] and, based on eq. (3), k_p^{app} is proportional to the square root of SW/V_{tot} .

The polymerization kinetics and linear molecular mass evolution with monomer conversion, illustrated in Fig. 1c and Fig. 2, result in polymers with low \bar{M}_w/\bar{M}_n values (Fig. 4a–c). Furthermore, \bar{M}_w/\bar{M}_n were dependent on SW , but still remained low, i.e., 1.14 at 87 % of monomer conversion ($SW/V_{tot} = 0.06 \text{ cm}^{-1}$) (Fig. 4c).

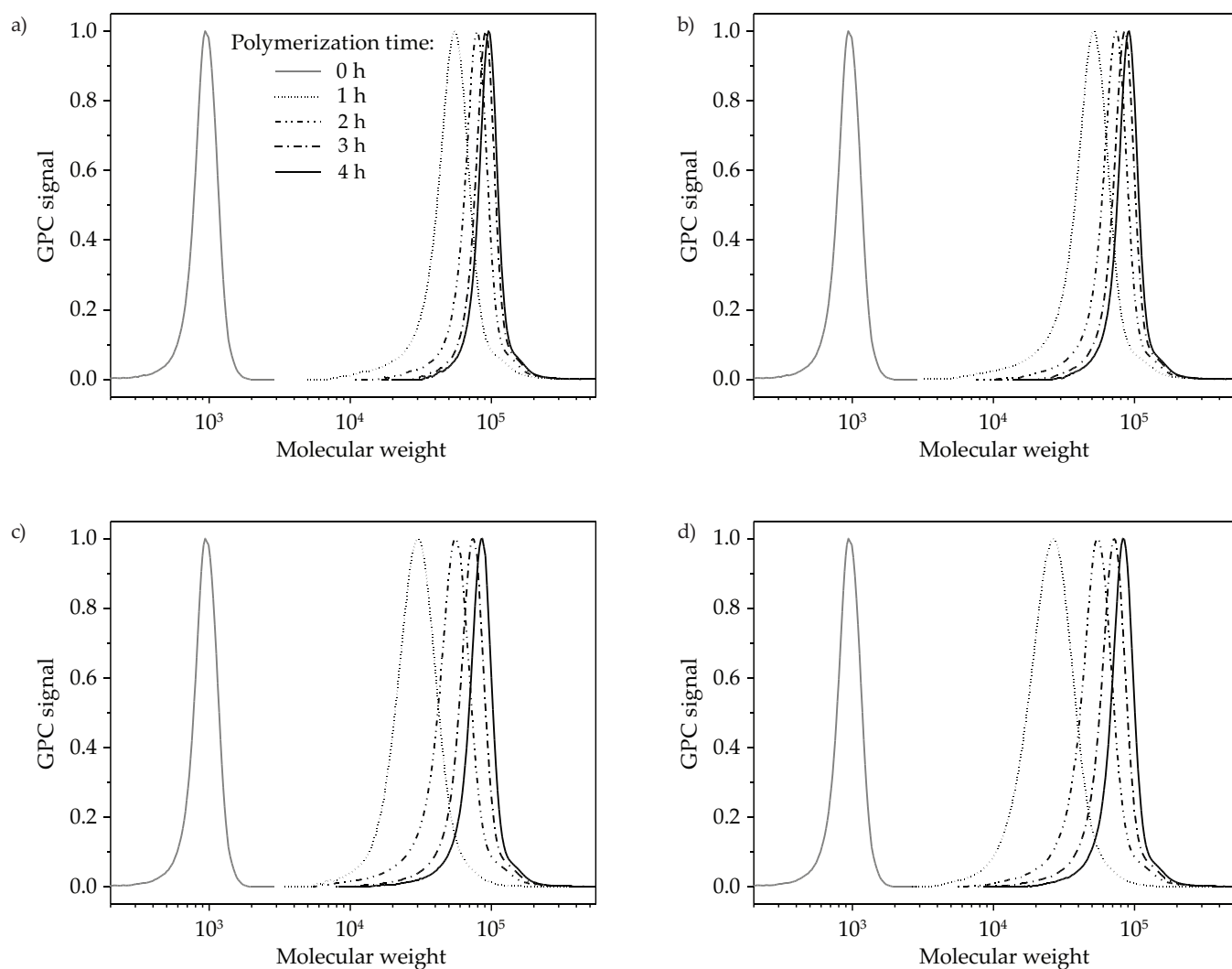


Fig. 4. GPC traces of OEGA polymerization in the presence of GL-Br₅ and their evolution over various times for the SW/V_{tot} ratio of: a) 0.31 cm⁻¹, b) 0.18 cm⁻¹, c) 0.06 cm⁻¹, d) 0.06 cm⁻¹ (for multi-step applied current electrolysis conditions)

Multi-step preparative electrolysis for *se*ATRP

Polymerization under constant current conditions was carried out and the results are reported in Table 1 (entry 4) and Fig. 5. The value of R_p showed a slight decrease from values observed under constant potential electrolysis conditions (compare k_p^{app} for entries 3 and 4 in Table 1). GPC analysis indicated a similar molecular weight evolution (Fig. 5) and narrow molecular weight distribution (Fig. 4c, d), and almost identical first-order kinetic plots were observed (Fig. 5). The differences between the theoretical and measured molecular weights originate from the different hydrodynamic radius of polymer stars and linear polymer standards for GPC.

To determine the arm lengths of the synthesized, high molecular mass, 5-arm star polymers, the arms were cleaved off the glucose core by acid solvolysis [41]. All results of the theoretical and expected DP_n values of the cleaved arms and the corresponding initiation efficiency (f_{IN}) are summarized in Table 1. These results (narrow

$\bar{M}_w/\bar{M}_n \leq 1.20$) confirm the absence of termination between growing arms, which means that all chains grow to approximately equal lengths, and therefore prove the absence of star-star coupling reactions. The initiation efficiency was close to 99 % (entries 1–4 in Table 1) [42].

Chemical structure of the glucose-based star polymers

The chemical structure of the GL-(POEGA-Br)₅ star polymer (Table 1, entry 4) was confirmed by ¹H NMR spectroscopy. In the ¹H NMR spectrum of GL-(POEGA-Br)₅ star-shaped polymer, shown in Fig. 6, the chemical shifts, 1.30–2.14 ppm, 2.19–2.50 ppm, 3.33–3.44 ppm, 3.45–3.58 ppm, 3.58–3.84 ppm, and 3.98–4.41 ppm, may be attributed to the –CH₂– (β), –CH– (α), –OCH₃ (e), –O–CH₂–CH₂–OCO– (f), –CH₂– from poly(ethylene glycol) backbone (g), and –O–CH₂–CH₂–OCO– (h) groups of POEGA units, indicating the presence of POEGA chains [30, 43, 44].

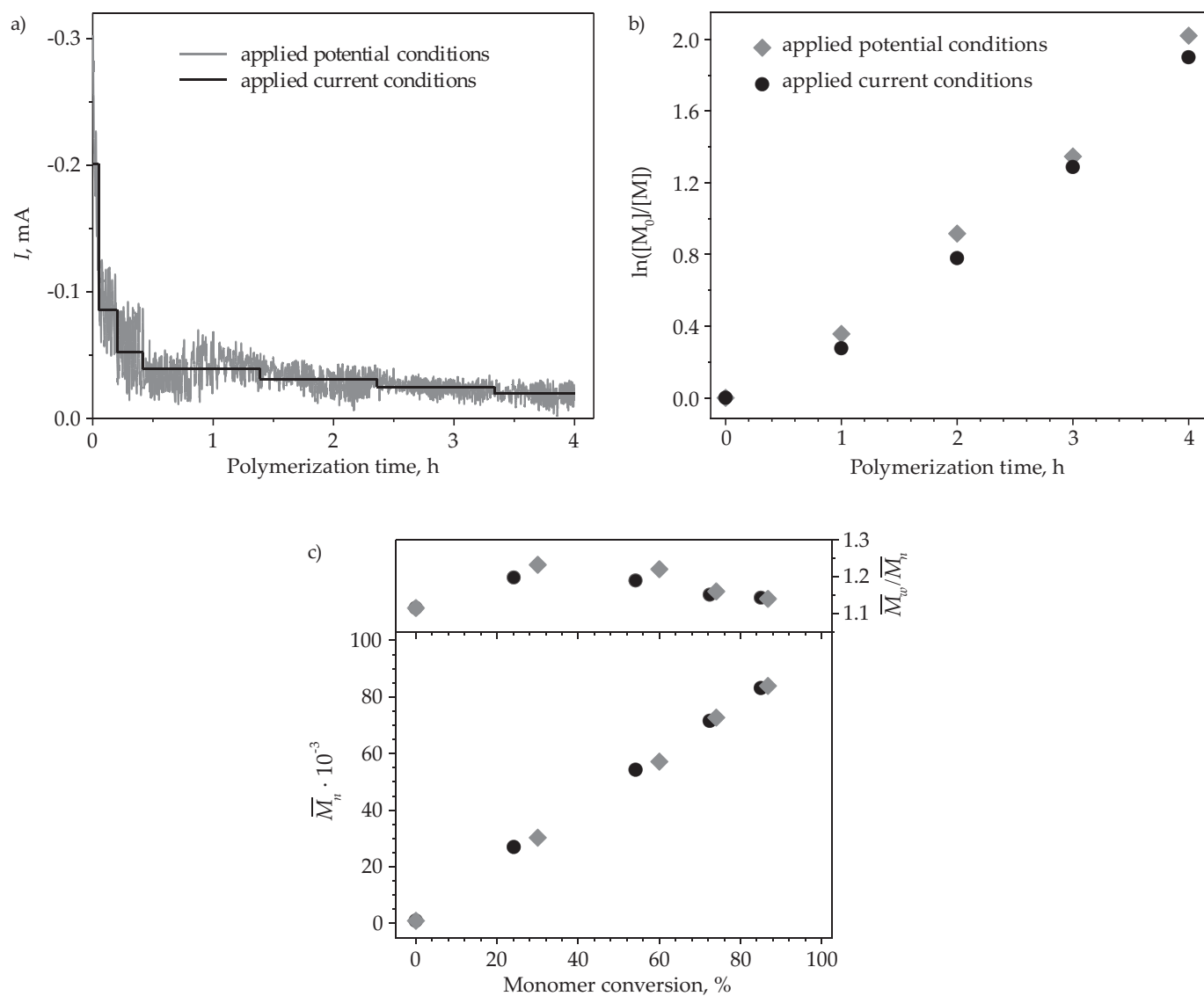


Fig. 5. Multi-step preparative electrolysis for *se*ATRP of GL-based star polymers: a) electrolysis results from applied potential conditions and applied current, b) first-order kinetic plot of monomer conversion *versus* polymerization time, c) \bar{M}_n and \bar{M}_w/\bar{M}_n *versus* monomer conversion (in electrolysis under constant potential and electrolysis under constant current conditions)

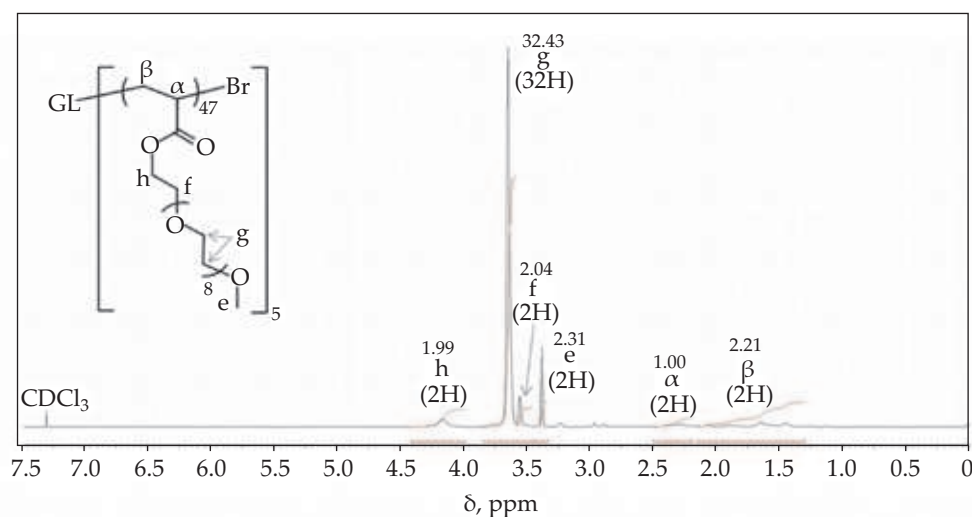


Fig. 6. ^1H NMR spectrum of GL-based star polymer (entry 4 in Table 1) after purification (in CDCl_3)

CONCLUSIONS

Well-controlled 5-arm hydrophilic polymers consisting of POEGA arms and α -D-glucose core were successfully obtained *via* improved simplified electrochemically mediated ATRP with 40 ppm of Cu^{II} complex. This appears to be the first report using improved *se*ATRP for the synthesis of GL-(POEGA-Br)₅ star polymers. Furthermore the possibility of reducing the size of the Pt cathode was demonstrated without significantly affecting the reaction rate under both constant potential and constant current conditions. The results from ¹H NMR spectral studies and GPC analyses confirm the controlled manner of the polymerization of OEGA. It is expected that these new star polymers may find application as drug delivery systems and antifouling coatings systems, resisting the fouling of biological media.

ACKNOWLEDGEMENT

Financial support from U-553/DS, U-718/DS, DS.CF.16.001, and U-771/DS/M is acknowledged. NMR spectra were recorded in the Laboratory of Spectrometry, Faculty of Chemistry, Rzeszow University of Technology and were financed from DS budget.

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Received 12 XII 2016.