Fig. 4. GPC traces of OEGA polymerization in the presence of GL-Br$_5$ 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

$\overline{M}_w/\overline{M}_n \leq 1.20$) 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 ^{1}H NMR spectroscopy. In the ^{1}H 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 $-CH_2-$ (β), $-CH-$ (α), $-OCH_3$ (e), $-O-CH_2-CH_2-OCO-$ (f), $-CH_2-$ from poly(ethylene glycol) backbone (g), and $-O-CH_2-CH_2-OCO-$ (h) groups of POEGA units, indicating the presence of POEGA chains [30, 43, 44].
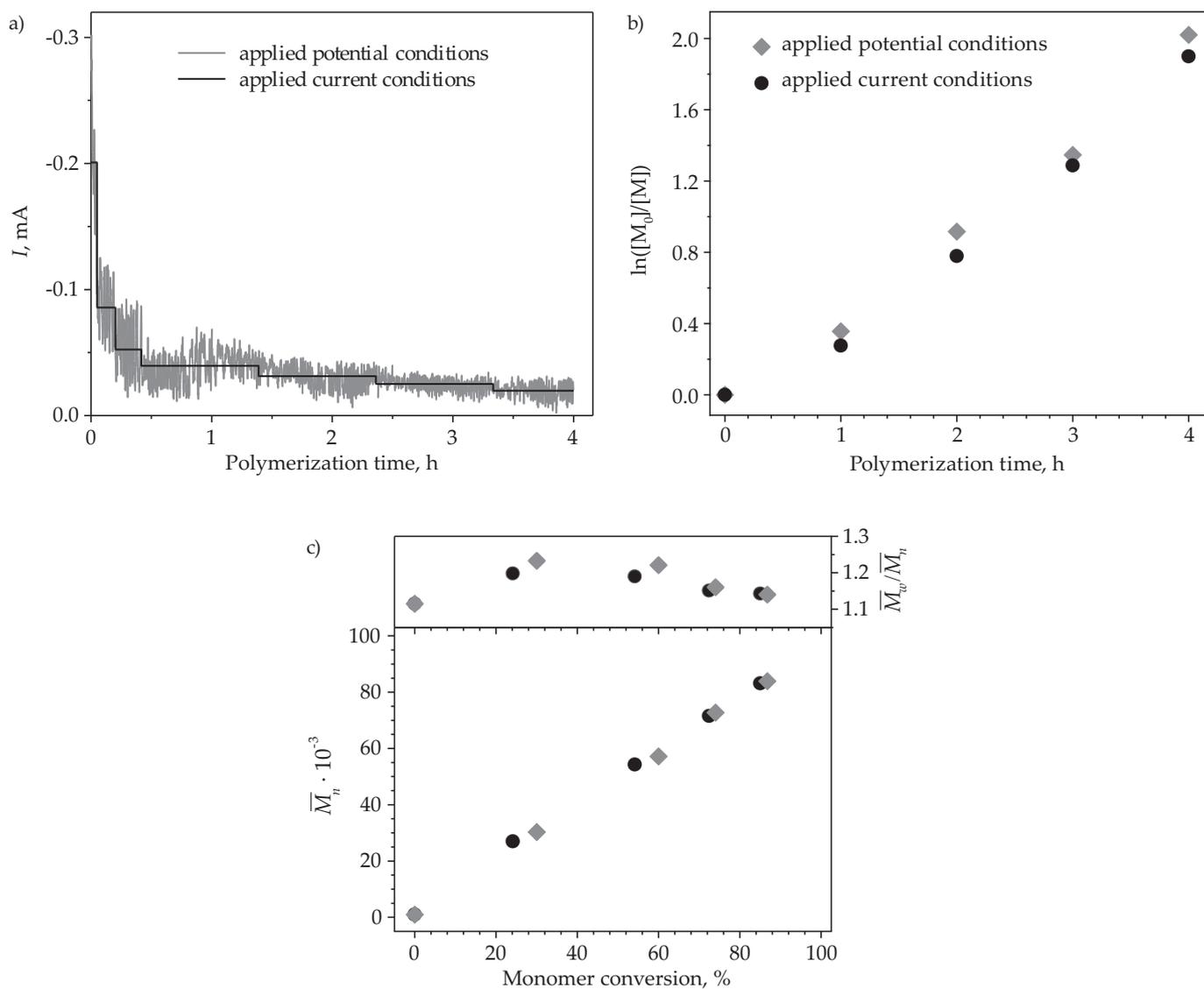
Fig. 5. Multi-step preparative electrolysis for *se*ATRP of GL-based star polymers: a) electrolysis results from applied potential conditions and applied current, b) first-order kinetic plot of monomer conversion *versus* polymerization time, c) $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ *versus* monomer conversion (in electrolysis under constant potential and electrolysis under constant current conditions)
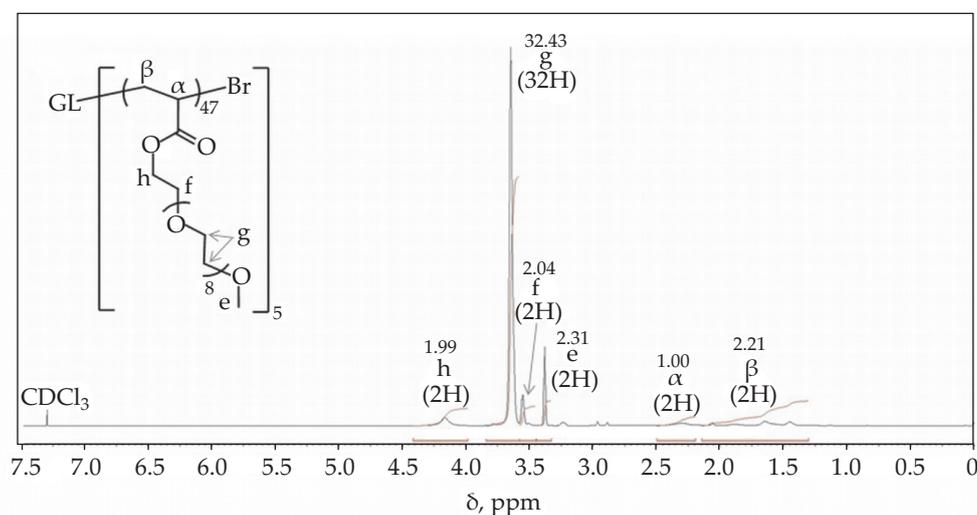

Fig. 6. ¹H NMR spectrum of GL-based star polymer (entry 4 in Table 1) after purification (in CDCl₃)