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

Paweł Chmielarz[1)]

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 (^{1}H 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 gwiaździstych 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 gwiaździste 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 (^{1}H NMR) i chromatografii żelowej (GPC) potwierdziły, że kontrolowana elektrochemicznie polimeryzacja OEGA przebiegała w sposób umożliwiający sterowanie tym procesem.

Słowa kluczowe: synteza polimerów, polimery gwiaździste 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 ($Cu^{II}Br_2$, 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 $Cu^{II}Br_2$ solution were prepared according to reference [33]. The 1,2,3,4,6-penta-*O*-isobutyryl bromide-α-D-glucose (GL-Br_5) 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

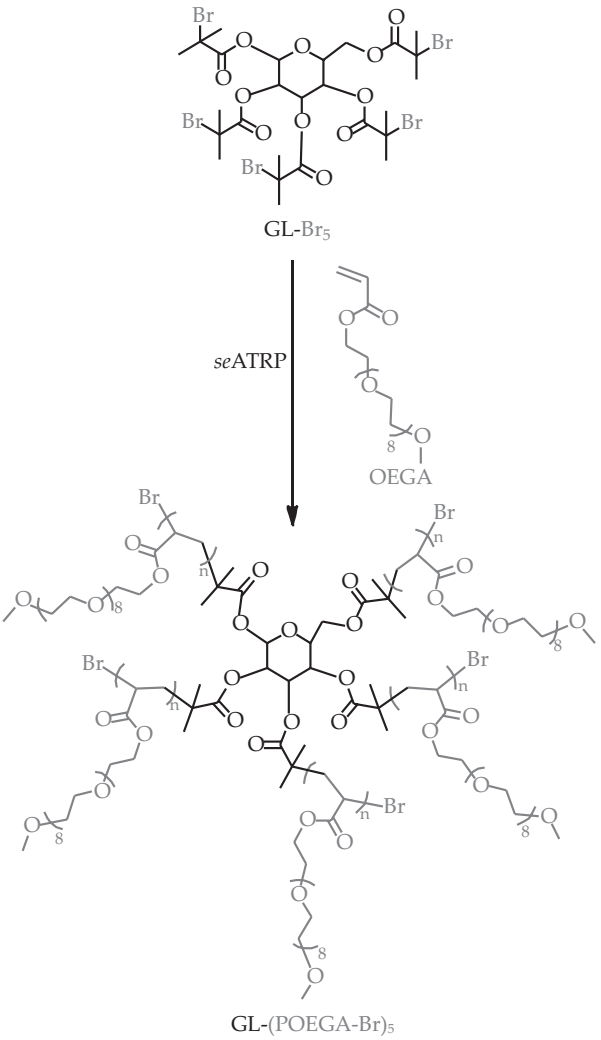
Nuclear magnetic resonance ^{1}H NMR spectra obtained in $CDCl_3$ were used for the calculations of monomer conversion and theoretical, number-average molecular weights ($\overline{M}_{n,th}$) after measurement on a Bruker Avance 500 MHz spectrometer according to previously described research [34]. Number-average 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* = 6.3–1.2 cm^2). The counter electrode was Al wire (l = 10 cm, d = 1 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