SYNTHESIS AND PROPERTIES OF CATIONIC CATECHOL BRUSH COPOLYMERS

Medeina Steponavičiūtė[1*], Vaidas Klimkevičius[1]

[1] *Institute of Chemistry, Vilnius University, Vilnius, Lithuania*
** e-mail: medeina.steponaviciute@chf.vu.lt*

Synthesis and application of bio-inspired polymeric materials have always been one of the main fields of materials science. In recent years, more and more attention has been given to mussel protein mimetic polymers containing catechol groups, known as the mussel-mimetic bioadhesives. These mussel-mimetic, polydopamine-containing polymers have been proven to be highly suitable for various applications in biomedicine such as biosensors, drug delivery, cancer cell imaging, medicine glue, hydrogel, and coatings [1]. Such extensive use of these biopolymers is due to their good antibacterial properties, complexation, and excellent adhesion to various surfaces and compounds under various environmental conditions [2]. In addition, they excel non-toxicity and biocompatibility [3].

Several different methods are used to obtain polymers with catechol moieties; however, the modification of preformed polymers by compounds carrying catechol groups remains supreme mainly due to the wide choice of starting polymer base and a wider possible choice of compounds suitable for the modification. Furthermore, this method gives materials with the catechol pendants along the entire length of polymer chains, and required catechol derivatives can be easily introduced on synthetic polymers by using simple synthetic strategies that allow straightforward functionalization [4]. Among synthetic polycations, poly(N,N-dimethylaminoethyl methacrylate) (pDMAEMA) is of great importance. Because of the reactivity of its amino groups, this polymer has much potential for facile modification reactions. Modification of pDMAEMA and its copolymers with catechol bearing substitutes, called quaternization, gives cationic catechol-containing polymers. Moreover, it possesses responsiveness to pH, temperature, and ionic strength, which gives unique properties to DMAEMA (co)polymers and their modified derivatives [5].

In this study, we demonstrated possibilities to synthesize well-defined gradient cationic catechol brush copolymers p(QDMAEMA-*co*-PEO_{19}MEMA) with DP close to 100 and Đ less than 1.18 and characterized their properties by ^{1}H NMR, FT-IR, UV-vis spectroscopy, and water contact angle measurements. For attachment of catechol moieties, DMAEMA units of the copolymers were quaternized with 2-chloro-3,4-dihydroxyacetophenone (CCDP). We also report the optimized quaternization procedure of DMAEMA units in the copolymers, enabling us to reach the degree of quaternization up to 100 %. Particular focus was directed to the kinetics of the RAFT copolymerization of DMAEMA and PEO macromonomer. Kinetics of RAFT copolymerization were studied by size exclusion chromatography (SEC) and ^{1}H NMR, which allowed calculating copolymerization rate and the evolution of copolymer composition during copolymerization. In addition, molecular weight M_n and dispersity Đ of the copolymers were determined by SEC with triple detection.

Acknowledgements. This project has received funding from European Social Fund (project No 09.3.3-LMT-K-712-19-0012) under grant agreement with the Research Council of Lithuania (LMTLT).

References

1. R. D. Balkenende, S. M. Winklera, P. B. Messersmith. Eur. Polym. J. **116** (2019) 134.
2. P. K. Forooshani., B. P. Lee. J. Polym. Sci. Part A Polym. Chem. **55** (2017) 9.
3. N. Patil, C. Jérôme, C. Detrembleur. Prog. Polym. Sci. **82** (2018) 34.
4. S. Moulay. Polym. Rev. **54** (2014) 436.
5. A. Muñoz-Bonilla, M. Fernández-García. Prog. Polym. Sci. **37** (2012) 281.