KINETICS OF OXYGEN-TOLERANT PHOTO-ATRP OF 2-HYDROXYETHYL METHACRYLATE

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Atom transfer radical polymerization (ATRP) is a robust polymerization technique to synthesize polymers with control molar mass, polydispersity, architecture, and end-group functionality. However, ATRP has some drawbacks such as using a high amount of catalyst and sensitivity towards oxygen. Purification of the final product from catalyst and removal of oxygen before polymerization using deoxygenation techniques (freeze pump thaw cycles and/or inert gas purging) are costly and time-consuming processes. Recently considerable attention has been directed towards oxygen-tolerant ATRP aiming to use ppm level of catalyst and eliminate the deoxygenation techniques[1]. Photo-ATRP is receiving significant notice due to its low cost of operation, using ppm level of catalyst, tolerance towards oxygen, the accurate control of reaction time, mild reaction conditions, and elimination of need to use additional chemicals[2]. However, photo-ATRP still has a long way to go which includes a mechanism, kinetics study, although a few achievements have already been made[3-4]. Here, the focus is an investigation of oxygen tolerant photo-ATRP of 2-hydroxyethyl methacrylate (HEMA). Detailed kinetic studies, including the effect of monomer to solvent ratio, a different type of initiators, a ligand to $CuBr_2$ ratio, amount of $CuBr_2$, a different type of ligands, monomer to initiator ratio, and the polymerization behaviors using various solvents were evaluated. It was found that photo-ATRP using 25-200 ppm catalyst loading with 2 equivalent of PMDETA in DMSO provided poly(2-hydroxyethyl methacrylate) with low dispersity ($Mw/Mn < 1.2$), linear dependences of both the first order kinetics and molar mass (Mn) with HEMA conversion. The polymerization of HEMA can be conducted even using only 25 ppm of $CuBr_2$ catalyst.

The authors thank grant agencies for financial support through projects APVV-19-0338, VEGA 2/0129/19. This work was performed during the implementation of the project Building-up Centre for advanced materials application of the Slovak Academy of Sciences, ITMS project code 313021T081 supported by the Integrated Infrastructure Operational Programme funded by the ERDF.

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