Warsaw, 11.09.2023

M. Sc. Eng. Dominik Wołosz

Faculty of Chemistry

Chair of Polymer Chemistry and Technology

Warsaw University of Technology

ABSTRACT OF THE DISSERTATION

„Studies on the synthesis and properties of isocyanate-free polyurethanes"

Dissertation supervisor: Prof. Paweł Parzuchowski

Assistant supervisor: Dr Magdalena Mazurek-Budzyńska

Typical synthetic methods towards polyurethanes' (**PUR**) concern the step-growth polyaddition of an oligodiol (oligoester diol, oligoether diol, or oligocarbonate diol), a diisocyanate and a chain extender (low-molar-mass α,ω-diol or α,ω-diamine). However, due to the toxicity of diisocyanates, alternative synthesis methods leading to the so-called isocyanate-free **PUR** (**NIPU**) are currently being sought.

The essential scientific aim of the dissertation was to develop innovative methods towards **PUR** materials, eliminating the use of diisocyanates. It was focused around two research threads: (1) the studies on the synthesis and analysis of the structure and properties of isocyanate-free poly(carbonate-urethane)s (**NIPCU**), exhibiting attractive mechanical and thermal properties, obtained based on the transurethane polycondensation process, and (2) the research on the synthesis and analysis of the structure and properties of unique isocyanate-free hydrophobically modified ethoxylated poly(hydroxy-urethane)s (**IFHEUR**) obtained via step-growth polyaddition and reactive extrusion (**REX**) processes, and then testing the aqueous solutions of **IFHEURs** as potential associative thickeners.

The established strategy leading to the synthesis of **NIPCUs** and **IFHEURs**, in conformity with the principles of sustainable development, assumed indirect management of a renewable raw material – carbon dioxide (CO_2) – as well as the use of the highest possible number and amount of bio-monomers, and also limiting the use of volatile organic solvents.

In the first section of the research, **NIPCU** was synthesized via the transurethane polycondensation between the precursor of rigid segments (bis(methyl carbamate)'s derivative or bis(2-hydroxyethyl carbamate)) and the precursor of flexible segments (oligocarbonate diol). Thanks to the appropriate modification of the rigid segment precursor's structure, innovative aliphatic, aliphatic-alicyclic, or aliphatic-aromatic thermoplastic **NIPCUs** were obtained, exhibiting remarkable mechanical and thermal properties. It was proved that the structure and

the content of rigid and flexible segments strongly influenced the mechanical and thermal properties of **NIPCUs**. The mechanical properties of the obtained materials combined both high tensile strength (e.g. 43 MPa) and high elongation at break (e.g. 700%), which has not been described in the literature so far. Interestingly, the mechanical properties of the obtained **NIPCUs** were comparable to commercially available isocyanate-based poly(carbonate-urethane)s. Moreover, as a part of the studies, the effect of the length of hydroxyalkyl chains (C2-C10) in the structure of the rigid segment precursor and **NIPCU** on the course of side reactions leading to the formation of urea groups was examined. The spectroscopic analyses of the **NIPCUs** and distillates proved that only short 2-hydroxyethyl- and 4-hydroxybutyl carbamate moieties were prone to the intramolecular side reaction (back-biting) leading to the formation of urea groups. Model reactions explained that the urea moieties were converted into the urethane ones in the **NIPCU** structure due to the reaction with oligocarbonate diols. The hereby dissertation also presents innovative aliphatic-aromatic **NIPCUs**, being an alternative to one of the most commonly obtained industrial **PURs** based on 4,4'-diphenylmethane diisocyanate, as well as unique **NIPCUs** obtained from bio-fatty diamine (PRIAMINE 1075). Non-crosslinked structure of the obtained materials and their thermoplastic properties provide them a wide range of potential applications, analogous to the traditional isocyanate-based **PUR** materials.

In the second section of the research, a novel class of water-based associative thickeners based on poly(hydroxy-urethane)s – **IFHEUR** – was revealed. An environmentally-friendly alternative to the typical isocyanate-based materials has been developed. The **IFHEUR**'s syntheses were carried out based on the step-growth polyaddition process of bis(cyclic carbonate) and α,ω-diamine, as well as the **REX** process, thus solving the issues of overheating and mixing the viscous **IFHEUR** melt, and the kinetic limitation regarding to the aminolysis of five-membered cyclic carbonates. The unique **IFHEUR** architecture had a crucial influence on their rheological properties in aqueous solutions. Their viscoelastic properties were resembling to the intermolecular association in aqueous solutions, typical for standard systems obtained from diisocyanates. Unlike known isocyanate-based associative thickeners, **IFHEURs** contained hydroxyl groups in their side chains, which opened new possibilities towards their functionalization and adjustment of the rheological properties.

Keywords: Isocyanate-free polyurethanes, poly(carbonate-urethane)s, poly(hydroxy-urethane)s, associative thickeners, hydrophobically modified ethoxylated polyurethanes, carbon dioxide-based polymers, bio-based polymers.

Dominik Wołosz