

Short thesis for the degree of doctor of philosophy (PhD)

**Kinetic study of reactions between industrially
important polyols and phenyl isocyanate**

by Bence Vadkerti

Supervisor: Dr. Lajos Nagy



UNIVERSITY OF DEBRECEN

Doctoral School of Chemistry

Debrecen, 2023

1. Introduction and objectives

Recently, polyurethanes are one of the most intensely researched polymers in the world. The reason behind that is, these materials can be designed with versatile properties, which allows us a wide range of application in daily life. These polymers can be used, for example, as insulation of houses, materials of quality mattresses, or even gaskets.

Application of products is greatly influenced by the reactants used in synthesis. Urethane bond is formed between isocyanates and alcohols in a nucleophilic addition reaction, and depending on the functionality of the reactants linear or crosslinked products can be obtained. By selecting the alcohol (mostly polypropylene glycol or an ethoxylated/propoxylated polyol) and the isocyanate (aromatic or aliphatic), the properties and the application field of the products are virtually determined. However, fine-tuning of the material could still occur by means of different additives, such as crosslinking agents. The quantity and quality of crosslinking agents significantly affect the mechanical properties of the product, hence these parameters can be varied depending on the application (e.g. bed mattresses, chair-backs, car seats) of the products.

Nevertheless, higher functionality of crosslinking agents does not necessarily mean that the molecule is able to form more crosslinks, since reactivity difference of functional groups can be significant, or reactivities can change during the reaction. As a consequence, the quality of the final product could be inadequate, or design of mechanical properties of polyurethanes could be less efficient.

My aim was to determine the reactivity of 8 industrially applied polyols and compare them. In addition, my goal was also to calculate the kinetically equivalent functionality values, by means of which the number of crosslinks formed in the syntheses can be estimated. Among to polyols investigated could be found simple, multifunctional alcohols (pentaerythritol, trimethylolpropane, glycerol), a sugar alcohol (sorbitol),

a carbohydrate (sucrose), and alkoxyated oligomers (pentaerythritol ethoxylate/propoxylate, Petol PA 500-5D), respectively.

2. Reaction conditions, applied equipment and methods

The reactions

During my work, polyols were reacted by phenyl isocyanate, which was used as a model compound to simulate reactions with industrially applied aromatic isocyanates. Reactions were carried out in high alcohol or isocyanate excess, in order to create pseudo-first order kinetics. Solvent of the reactions was dimethyl sulfoxide, the reactions were thermostated at 30 °C, and kept under nitrogen or argon atmosphere. After pre-determined time intervals samples were taken out from the reaction mixture and were quenched in methanol. Samples from reactions providing high amount of reaction products were derivatized by p-tolyl isocyanate in the presence of catalyst before mass spectrometric measurements. In the case of sucrose, temperature dependence of the reaction was also investigated in the range of 30 – 60 °C.

Applied equipment and methods

In the case of high polyol excess, monitoring of the reactions occurred by HPLC-UV. For high isocyanate excess, reactions that formed less amount of reaction products were also studied by HPLC-UV, while reactions providing high amount of reaction products were investigated by MALDI-TOF-MS. Evaluation of the results was done by softwares from Bruker (DataAnalysis 3.4 and FlexAnalysis).

The assignment of rate constants to the corresponding hydroxyl groups was aided by NMR measurements and DFT calculations.

3. New scientific results

3.1. Reactivity of glycerol, pentaerythritol, and trimethylolpropane was determined. It was proved in the case of glycerol that relative reactivities were virtually independent of which reactant was applied in high excess. Kinetically equivalent functionality of glycerol was calculated.

In the case of polyol excess, it was determined that glycerol's primary hydroxyl groups are nearly four times more reactive than the secondary one. In addition, reactivity of hydroxyl groups of trimethylolpropane (TMP) and pentaerythritol (PE) was calculated, and TMP was proved to be more reactive approximately with 20%. The result was explained by their molecular structure differences. It was also demonstrated that glycerol's primary hydroxyl groups, as well as hydroxyl groups of TMP and PE possessed similar reactivity. Moreover, it was proved that reactivity of hydroxyl groups significantly decreases with the reaction in the case of high isocyanate excess, due to steric and inductive effects.

Comparing relative reactivities of glycerol's primary and secondary groups for isocyanate and polyol excess demonstrated that they were nearly the same. The results were 3.94 (isocyanate excess) and 3.83 (polyol excess).

Having calculated the rate constants of glycerol, kinetically equivalent functionality could be calculated for glycerol. The results unambiguously showed us that glycerol was a bifunctional (chain extender) molecule under both reaction conditions. The functionality of the molecule was 2.26.

3.2. Pseudo-first order rate constants and kinetically equivalent functionality values of sorbitol and sucrose were calculated for isocyanate and polyol excess. Rate constants were unambiguously assigned to the corresponding hydroxyl groups. It was proved that increasing temperature favoured the formation of crosslinks.

The calculated rate constants in the case of polyol excess proved that reactivity of primary hydroxyl groups of sorbitol and sucrose were the same order of magnitude that of glycerol's.

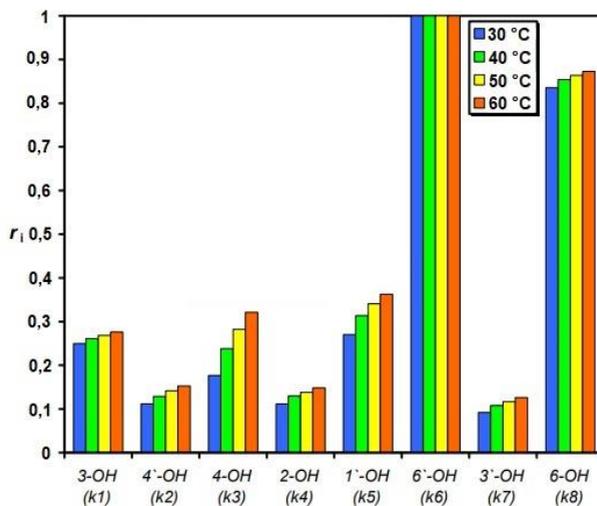
Similarly to glycerol, isocyanate excess showed a sharp decrease in reactivity of hydroxyl groups, which was also explained by steric and inductive effects. Kinetically equivalent functionality values were calculated for sorbitol and sucrose. The results demonstrated that, while sorbitol acted as a bifunctional molecule (chain extender), sucrose was a trifunctional compound (crosslinker).

Rate constants of sorbitol and sucrose were successfully assigned to the corresponding hydroxyl groups by tandem mass spectrometry, two-dimensional NMR, and DFT calculations. By means of the results reactivity order of hydroxyl groups were determined in both molecules.

Reaction of sucrose and phenyl isocyanate was also carried out at 30, 40, 50 and 60 °C, results of which proved that increasing temperature favoured the formation of crosslinks.

Table 1: Calculated rate constants for sorbitol and sucrose

	Sorbitol ($k \times 10^2$)		Sucrose ($k \times 10^2$)	
	Polyol excess	Isocyanate excess	Polyol excess	Isocyanate excess
k_1	0.93	41.56	1.11	26.26
k_2	1.19	19.5	0.59	16.89
k_3	0.98	4.45	1.03	9.33
k_4	0.64	1	0.5	4.66
k_5	6.91	0.24	1.36	2.04
k_6	8.43	0.07	4.45	0.96
k_7	-	-	0.41	0.32
k_8	-	-	3.72	0.06

**Figure 1:** The effect on reactivity of sucrose's hydroxyl groups by varying temperature

3.3. Rate constants for pentaerythritol-ethoxylate, pentaerythritol-propoxylate, and Petol PA 500-5D were determined. It was proved that by using the alkoxyated oligomers, steric and inductive effects were less considerable in the reactions using high isocyanate excess.

It was proved that ethoxylated pentaerythritol had higher reactivity than the propoxylated one. The reason behind the decreased reactivity was the presence of secondary hydroxyl groups in the propoxylated oligomer, amount of which was calculated by NMR measurements. The primary – secondary hydroxyl group ratio in the propoxylated pentaerythritol was 16% - 84%. The results clearly showed that pentaerythritol was more reactive than its alkoxyated derivatives.

Reactivity of hydroxyl groups in the alkoxyated oligomers decreased less compared to the smaller polyols. This result proved that by the incorporation of oligomer chains into the polyol, reacting functional groups got so far from each other that steric and inductive effects had less influence on the reactivity of hydroxyl groups.

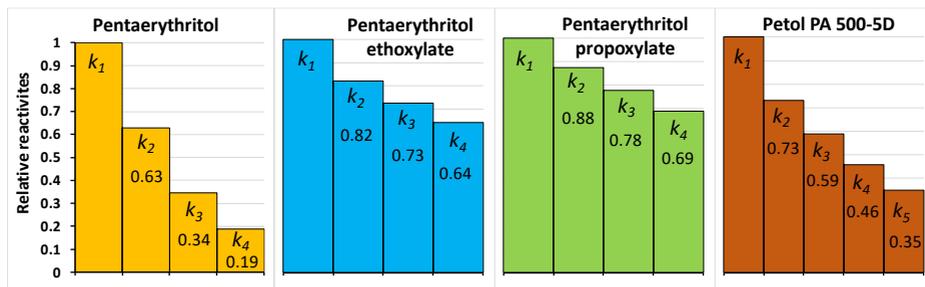


Figure 2: Relative reactivities in pentaerythritol and alkoxyated oligomers

4. Possible applications of the results

Experiments with polyurethanes are one of the most prominent areas of modern polymer chemistry research. Due to their versatile properties many applications of polyurethanes are well known. In order to design polymers, it is crucial to investigate the chemical reactions occurring during the synthesis. From these studies, valuable information can be obtained such as relative reactivities of the functional groups, or the average amount of crosslinks that can be formed during crosslinking processes.

My results could be guides for those researchers who work in this field of topic, and on the other hand, they could help to the industry designing new kind of products. Moreover, these data could be valuable for the production of biocompatible, biodegradable or even shape-memory polymers, application of which plays a key role recently for example in medical science where design of properties is essential.



Registry number: DEENK/356/2023.PL
Subject: PhD Publication List

Candidate: Bence Vadkerti
Doctoral School: Doctoral School of Chemistry
MTMT ID: 10077886

List of publications related to the dissertation

Foreign language scientific articles in international journals (3)

1. **Vadkerti, B.**, Juhász, A., Lakatos, C., Zsuga, M., Kéki, S., Nagy, L.: Reactivity of multi-arm polyols towards isocyanates.
New J. Chem. 46, 9871-9879, 2022. ISSN: 1144-0546.
DOI: <https://doi.org/10.1039/D2NJ01103D>
IF: 3.3
2. Nagy, L., **Vadkerti, B.**, Lakatos, C., Fehér, P. P., Zsuga, M., Kéki, S.: Kinetically Equivalent Functionality and Reactivity of Commonly Used Biocompatible Polyurethane Crosslinking Agents.
Int. J. Mol. Sci. 22 (8), 1-19, 2021. ISSN: 1661-6596.
DOI: <http://dx.doi.org/10.3390/ijms22084059>
IF: 6.208
3. Nagy, L., **Vadkerti, B.**, Batta, G., Fehér, P. P., Zsuga, M., Kéki, S.: Eight out of eight: a detailed kinetic study on the reactivities of the eight hydroxyl groups of sucrose with phenyl isocyanate.
New J. Chem. 43 (38), 15316-15325, 2019. ISSN: 1144-0546.
DOI: <http://dx.doi.org/10.1039/C9NJ03569A>
IF: 3.288

List of other publications

Foreign language scientific articles in international journals (4)

4. Závori, L., Molnár, T., Várnai, R., Kanizsai, A., Nagy, L., **Vadkerti, B.**, Szirmay, B., Schwarcz, A., Csécsesi, P.: Cystatin-c May Indicate Subclinical Renal Involvement, While Orosomucoid Is Associated with Fatigue in Patients with Long-COVID Syndrome.
J. Pers. Med. 13 (2), 1-8, 2023. EISSN: 2075-4426.
DOI: <http://dx.doi.org/10.3390/jpm13020371>





5. Lakatos, C., Kordován, M. Á., Czifrák, K., Nagy, L., **Vadkerti, B.**, Daróczi, L., Zsuga, M., Kéki, S.:
Synthesis of Sucrose-HDI Cooligomers: new Polyols for Novel Polyurethane Networks.
Int. J. Mol. Sci. 23 (3), 1-13, 2022. ISSN: 1661-6596.
DOI: <http://dx.doi.org/10.3390/ijms23031444>
IF: 5.6
6. Nagy, L., Kuki, Á., Nagy, T., **Vadkerti, B.**, Erdélyi, Z., Kárpáti, L., Zsuga, M., Kéki, S.: Encoding
Information into Polyethylene Glycol Using an Alcohol-Isocyanate "Click" Reaction.
Int. J. Mol. Sci. 21 (4), 1-9, 2020. ISSN: 1661-6596.
DOI: <http://dx.doi.org/10.3390/ijms21041318>
IF: 5.924
7. Nagy, L., Nagy, M., **Vadkerti, B.**, Daróczi, L., Deák, G., Zsuga, M., Kéki, S.: Designed
Polyurethanes for Potential Biomedical and Pharmaceutical Applications: Novel Synthetic
Strategy for Preparing Sucrose Containing Biocompatible and Biodegradable Polyurethane
Networks.
Polymers. 11 (5), 1-19, 2019. EISSN: 2073-4360.
DOI: <http://dx.doi.org/10.3390/polym11050825>
IF: 3.426

Hungarian abstracts (8)

8. **Vadkerti, B.**, Juhász, A., Lakatos, C., Zsuga, M., Kéki, S., Nagy, L.: Polimer polioloak és fenil-
izocianát reakcióinak kinetikai vizsgálata = Kinetic study of reactions of polymer polyols and
phenyl-isocyanate.
In: XXVIII. Nemzetközi Vegyészkonferencia = 28th International Conference on Chemistry.
Ed.: Majdik Kornélia, Erdélyi Magyar Műszaki Tudományos Társaság, Kolozsvár, 43, 2022,
(ISSN 2734-7109) ISBN: 27347109
9. **Vadkerti, B.**, Nagy, L., Lakatos, C., Fehér, P. P., Zsuga, M., Kéki, S.: Ipari térhálósítók kinetikai
funkcionalitásának és reaktivitásának meghatározása = Determination of kinetic functionality
and reactivity of crosslinkers used in industry.
In: XXVII. Nemzetközi Vegyészkonferencia = 27th International Conference on Chemistry.
Ed.: Majdik Kornélia, Erdélyi Magyar Műszaki Tudományos Társaság, Kolozsvár, 1, 2021,
(ISSN 2734-7109)
10. Nagy, L., **Vadkerti, B.**, Juhász, A., Lakatos, C., Zsuga, M., Kéki, S.: Négy- és ötkarú polimer
polioloak reaktivitásának vizsgálata fenil-izocianát jelenlétében = Reactivity of four- and five-
arm industrially important polymerpolyols in the presence of phenyl isocyanate.
In: XXVII. Nemzetközi Vegyészkonferencia = 27th International Conference on Chemistry.
Ed.: Majdik Kornélia, Erdélyi Magyar Műszaki Tudományos Társaság, Kolozsvár, 1, 2021,
(ISSN 2734-7109)





11. Lakatos, C., Kordován, M. Á., Czifrák, K., Nagy, L., **Vadkerti, B.**, Zsuga, M., Kéki, S.: Új típusú szacharóz-hexametilén-diizocianát (HDI) oligomer tartalmú poliuretánok előállítása és vizsgálata = Synthesis and characterization of new types of polyurethanes containing sucrose-hexamethylene diisocyanate (HDI) oligomer.
In: XXVII. Nemzetközi Vegyészkonferencia = 27th International Conference on Chemistry.
Ed.: Majdik Kornélia, Erdélyi Magyar Műszaki Tudományos Társaság (EMT), Kolozsvár, 1, 2021, (ISSN 2734-7109)
12. Kordován, M. Á., Nagy, L., **Vadkerti, B.**, Batta, G., Fehér, P. P., Zsuga, M., Kéki, S.: A biokompatibilis poliuretán alapú polimerek térhálósítójaként használt szacharóz reaktivitásának vizsgálata fenil-izocianát jelenlétében.
In: Biotechnológia a Debreceni Egyetemen Tudományos szimpózium: Program és összefoglalók, Debreceni Egyetem Természettudományi és Technológiai Kar Biotechnológiai Intézet, Debrecen, 37, 2019.
13. **Vadkerti, B.**, Nagy, L., Batta, G., Fehér, P. P., Zsuga, M., Kéki, S.: A szacharóz reakciója fenil-izocianáttal = The Reaction of Sucrose with Phenyl-isocyanate.
In: XXV. Nemzetközi Vegyészkonferencia = 25th International Conference on Chemistry.
Szerk.: Majdik Kornélia, Erdélyi Magyar Műszaki Tudományos Társaság, Kolozsvár, 63, 2019, (ISSN 1843-6293)
14. **Vadkerti, B.**, Nagy, L., Nagy, M., Daróczy, L., Deák, G., Zsuga, M., Kéki, S.: Szacharóz tartalmú poliuretán scaffoldok előállítása és karakterizálása.
In: Biotechnológia a Debreceni Egyetemen Tudományos szimpózium : Program és összefoglalók, Debrecen Egyetem, Debrecen, 26, 2019.
15. Kordován, M. Á., Nagy, L., Nagy, M., **Vadkerti, B.**, Daróczy, L., Deák, G., Zsuga, M., Kéki, S.: Új típusú poliuretánok előállítása szacharóz, 1,6-hexametilén diizocianát (HDI) és (epszilon)-kaprolakton felhasználásával = Preparation of New Type Polyurethanes Containing Sucrose, 1,6-hexamethylene Diisocyanate (HMDI) and epsilon-Caprolacton.
In: 25th International Conference on Chemistry = XXV. Nemzetközi Vegyészkonferencia.
Szerk.: Majdik Kornélia, Erdélyi Magyar Műszaki Tudományos Társaság (EMT), Kolozsvár, 55, 2019, (ISSN 1843-6293)

Foreign language abstracts (3)

16. **Vadkerti, B.**, Nagy, L., Kuki, Á., Nagy, T., Erdélyi, Z., Kárpáti, L., Zsuga, M., Kéki, S.: Information coding by peg - aliphatic isocyanate reaction and decoding by maldi-tof ms.
In: International Mass Spectrometry Conference 2022 : Poster Abstract book, [S. n.], Maastricht, 51, 2022.
17. Lakatos, C., Kordován, M. Á., Czifrák, K., Nagy, L., **Vadkerti, B.**, Daróczy, L., Zsuga, M., Kéki, S.: Monitoring and characterization of sucrose-HDI cooligomer formation by MÅLDI-TOF mass spectrometry.
In: International Mass Spectrometry Conference 2022 : Poster Abstract book, [S. n.], Maastricht, 49-50, 2022.





18. **Vadkerti, B.**, Nagy, L., Batta, G., Fehér, P. P., Zsuga, M., Kéki, S.: Determination of relative reactivity of hydroxyl groups in sucrose.

In: Young Researchers' International Conference on Chemistry and Chemical Engineering: Program and Abstracts, Babes-Bolyai University, Faculty of Chemistry and Chemical Engineering, Cluj-Napoca, 31, 2021.

Total IF of journals (all publications): 27,746

Total IF of journals (publications related to the dissertation): 12,796

The Candidate's publication data submitted to the iDEa Tudóstér have been validated by DEENK on the basis of the Journal Citation Report (Impact Factor) database.

24 July, 2023

