SCREENING OF ENZYME-CATALYZED POLYCONDENSATION OF BIO-BASED MONOMERS IN SOLUTION

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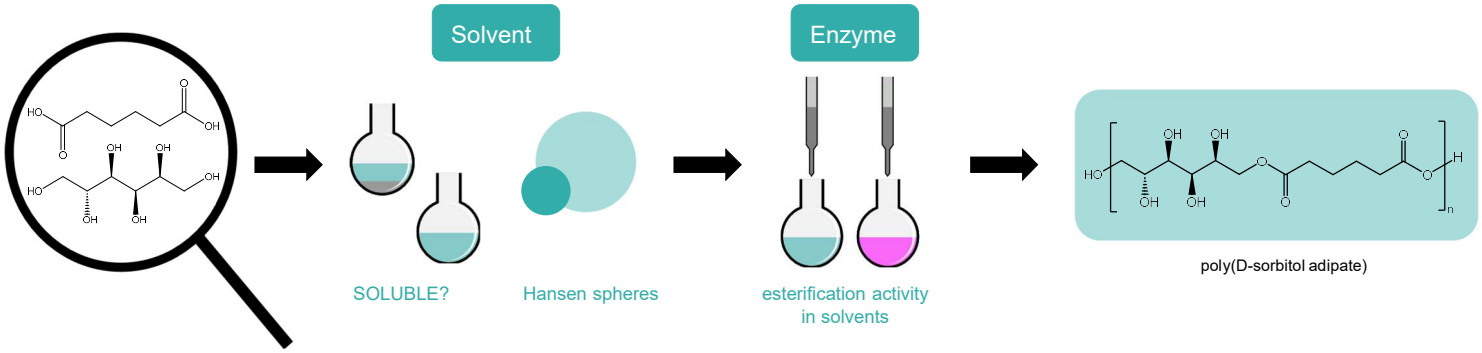


Conclusion

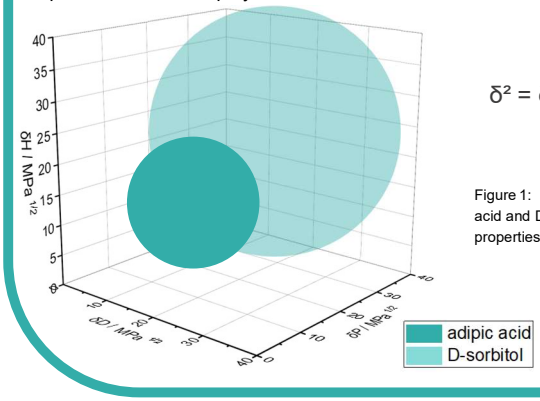
- **Biobased monomers are characterized by Hansen solubility parameters facilitating the selection of solvents for the enzyme-catalyzed polyester synthesis.**
- **The determination of esterification activity of lipase B of *Candida antarctica* provides information on the compatibility of solvents and the enzyme.**
- **Selected evaluation tools proofed to be time- and resource-saving and provide an overview of solvents to be examined in up-scaled synthesis reactions.**

Introduction

Polyesters are conventionally synthesized *via* melt-polycondensation using metal-based catalysts and high temperatures of 140 °C to 280 °C. Such temperatures, however, interfere with linear chain growth when using multifunctional green monomers such as D-sorbitol due to side reactions such as dehydrations. An effective approach to lower the required reaction temperature is the use of lipases, such as lipase B of *Candida antarctica* (CALB), which is commonly immobilized on carriers like Immobead-150 (CALB-IB150). As bio-based monomers often have melting points of above 100 °C, a solvent must be used to achieve a homogeneous reaction mixture and promote esterification. As the selected solvent must not inhibit the enzyme activity, suitable solvents should be identified and carefully examined.

Hansen solubility parameters as a tool to evaluate the solubility of monomers

One of the prime characteristics of solvents is their ability to dissolve a specific substrate. This can be described using the solubility parameters (δ), which describe dispersion forces (*D*), polar forces (*P*) and hydrogen-bonding (*H*) [1]. To determine the solubility parameters, 10 *wt*.% adipic acid or D-sorbitol are stirred in different solvents for 24 h at room temperature. Hansen spheres of these two monomers (Fig. 1) only slightly overlap and dimethylformamide and dimethyl sulfoxide are identified as common solvents. As a result, green solvents which only dissolve adipic acid are selected for further investigation as partial dissolution of monomers is expected to be sufficient based on experiences in mass polycondensations.

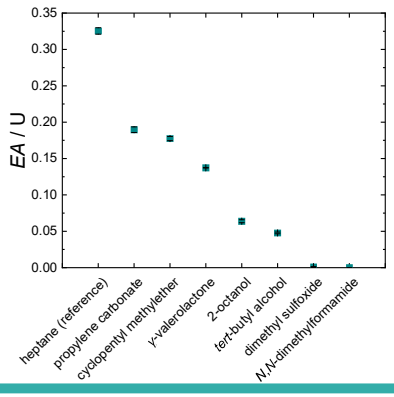


$$\delta^2 = \delta D^2 + \delta P^2 + \delta H^2$$

Figure 1: Hansen spheres of adipic acid and D-sorbitol, used for estimating properties of common solvents.

Esterification activity of CALB-IB150 in different solvents

Another prime feature of a solvent is its interaction with the immobilized enzyme. For the evaluation of the esterification activity (*EA*) of CALB-IB150, 10 mg immobilized catalyst are used to esterify 0.13 M butyric acid and 0.3 M butanol in different solvents at 50 °C. The amount of butyl butyrate formed is determined after 2 h *via* titration against ethanolic NaOH solution and the results are given in U (µmol min^{-1} mg^{-1} catalyst, method adjusted from [2]). By using this method, clear differences in activity of the enzyme in different solvents are determined (Fig. 2). As an example, while the enzyme performs better in heptane than other solvents like propylene carbonate, greener solvents are preferrable.



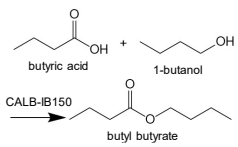


Figure 2: Results of the examination of esterification activity of CALB-IB150 in different solvents.

Examination of the esterification of adipic acid and D-sorbitol

The polycondensation of adipic acid and D-sorbitol (ratio 0.95:1) using CALB-IB150 is examined in different solvents. Solvent selection is based on Hansen solubility test results and esterification activity determination, with particular emphasis on green solvents. Esterification has already been observed in preliminary polymerizations and the results hold significant potential for future screenings of polyester synthesis reactions.

References

[1] Hansen, C. M. (2007). Hansen solubility parameters: a user's handbook. CRC press.

[2] Kiran, K. R., Hari Krishna, S., Suresh Babu, C. V., Karanth, N. G., & Divakar, S. (2000). An esterification method for determination of lipase activity. *Biotechnology letters*, *22*, 1511-1514.

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Research on enzyme-catalyzed polycondensation

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