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3D Printing and a New Way to Synthesize Bio-Based and Biodegradable PLA in Chemistry Education for School Students

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Abstract Plastics are a central part of our everyday lives. One plastic is increasingly finding its way into daily use: polylactic acid (PLA). PLA is being used more and more, as it is an important component (polymer) of bio-based and biodegradable plastic. However, experimental access to plastics for students in school chemistry classes is usually tricky because the syntheses of plastics either are time-consuming or do not provide the intended results. Therefore, an experiment was developed that provides simple and quick access polymers and plastics. With this experiment, school students can independently synthesize polylactic acid in chemistry lessons.

Keywords: *polycondensation, polylactic acid, plastics, school experiment, 3D printing, circular economy*

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1. Introduction

Plastics are omnipresent in daily life and have countless applications, from plastic bottles to phone cases. For this reason, plastics as a topic are also a central component of chemistry education, for example, in German secondary schools [1]. One practical and contemporary teaching object of plastics in school is the 3D printer. Therefore, 3D printing is increasingly used in chemistry education [2,3,4,5,6,7].

The three-dimensional printing of plastics objects has many potential applications. One possibility is the quick and cheap printing of different structures (Figure 1), such as molecular models [4,5,6]. In addition, objects can be printed for laboratory, such as continuous flow reactors for photochemical reactions [7].This makes it possible to meet specific requirements and quickly test the application.

Another educational option is to give insights into how a 3D printer works or to analyze the chemical properties of the filaments (Figure 2) used.

3D printing uses the material properties of thermoplastics by applying the Fused Deposition Modeling (FDM) method. These material properties can be studied experimentally to help students understand better how printers work [3]. Previous work conducted by our research group has already provided insights into how the structure-properties relations of the filaments influence their use in 3D printing [3].

Besides the material properties, the primary material for most filaments is quite interesting for chemistry education. With the experiment presented in this article, we take a closer look at the polymer polylactide (PLA) and further address the synthesis of the primary material of filaments.

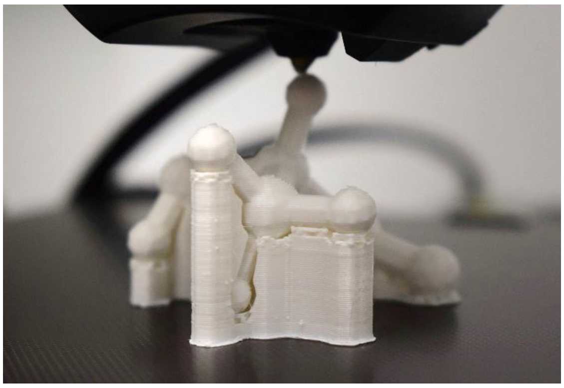

Figure 1. 3D printing of a lactic acid molecular model with support structure

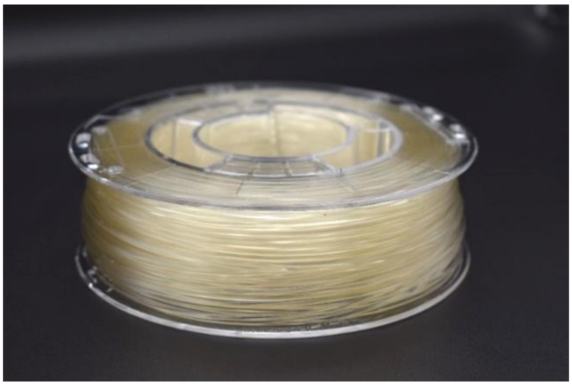

Figure 2. PLA, a typical filament for 3D printing

Although plastics are very useful, the many ecological problems they cause cannot be ignored. Littering and plastic pollution is a growing global concern. 3D printing, for example, creates plastic debris due to necessary support structures. Accordingly, the question arises about how we can act in a sustainable manner in the near future. Among other things, this sustainable action is set out in the UN's Sustainable Development Goals. Therefore, chemistry education should also address how chemistry can be greener and more sustainable [8,9]. One possibility is to address concepts such as circular economy and the circulation of plastics [10] in particular.

In the context of sustainability, it is worth drawing attention to a bio-based and biodegradable polymer polylactic acid (PLA) [11,12].

PLA is a typical filament used for 3D printing. It offers many advantages for printing, such as its low cost and easy processing [3] and the fact that it is a bio-based polymer [13,14]. The starting point of a cycle (circular economy) is the production of plastic. Therefore, in chemistry education that aims to address the concept of a circular economy, conducting experiments with PLA seems beneficial. However, this leads to the following questions: How can the students experiment with PLA themselves? Are there ways in which students can synthesize this polymer themselves?

2. Experimental Procedure

Student experiments on the synthesis of PLA can already be found in the literature [15,16,17]. However, these experiments have various difficulties. On the one hand, the chemical reaction products are difficult to compare with PLA, as the products are brownish to dark brown in color or the reaction product is not completely solid [15,16,18]. In addition, some of the reaction products smell strongly of caramel, which indicates various chemical side reactions. The "polylactic acid" produced in these experiments is only comparable to PLA-based plastics to a limited extent (Figure 3). On the other hand, some of these experiments require a drying oven and a long synthesis duration (24 hours) [15]. These experiments usually result in the same brownish product.

Figure 3. Usual results of experiments available in the literature

The fundamental problem is that the experiments that are presented in the literature take a very long time or the result is not comparable to PLA-based plastics. With the experimental procedure that we present here, we aimed to overcome these problems by providing an experiment with which students can synthesize PLA.

2.1. Chemicals and Reagents

2.1.1. Lactic Acid

The essential constituent of PLA is 2-hydroxypropanoic acid (lactic acid). The important feature of the reagent 2-hydroxypropanoic acid is that it combines two functional groups into the one molecule necessary for polycondensation to form a polyester: the hydroxyl and carboxyl groups .

Accordingly, the reaction conditions should be provided so that the lactic acid molecules react with each other to form an ester of carboxylic acid.

2.1.2. Catalyst

The catalyst used in the literature (zinc chloride or tin chloride) of chemistry education initiates the reaction of the lactic acid monomers to form the polymer [15]. However, the reaction product is not suitable for the production of plastics (Figure 3).

For this reason other catalysts are used in the industrial production of PLA [3,8]. For example, a frequently used catalyst combines tin(II) 2-ethylhexanoate with an alcohol [11,12,17,19]. In addition, lactide is usually the reactant. The reaction pathway of these syntheses is via the ring-opening polymerization (ROP) of the cyclic diester of lactic acid: the lactide (3,6-dimethyl-1,4-dioxane-2,5-dione) [17].

A comprehensive multi-step and demanding procedure is frequently implemented when introducing university students to organic chemistry [17]. However, easy-to-implement experimental instruction should be provided for student experiments in chemistry lessons. For example, on the basis of the catalyst of the ROP, a Petri dish synthesis could be developed and tested with school students, in which only the catalysts tin(II) 2-ethylhexanoate and isopropanol as well as heat are added to the lactic acid. In general, the school students should be advised to handle tin(II) 2-ethylhexanoate in a safety-conscious manner and to wear protective gloves. These reaction conditions allow the synthesis to take place (Figure 4).

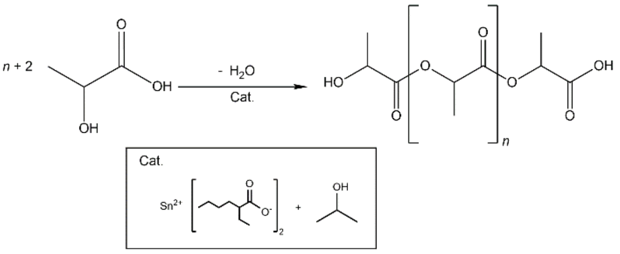

Figure 4. Simplified chemical equation of the ROP

For this purpose, a material-saving synthesis was developed that can be realized with a minimum of materials and can be easily reproduced by school students (appendix: worksheet). In addition, with this procedure, the formation of the polycondensate can already be observed after 25 min.

2.2. Student Experiment

First, the hot plate is heated to 175 °C. Then, 5 mL of the lactic acid and 0.5 mL of isopropanol are measured with pipettes and mixed in the glass Petri dish. Next, 0.5 mL of tin(II) 2-ethylhexanoate is added with another pipette. Finally, all substances are mixed carefully with the spatula and placed on the hot plate. After 10, 20, and 30 min, remove a small amount of the substance from the glass Petri dish with the spatula and place it, for example, on a slide. After cooling (approx. 2 min), check the solidity of the product on the slide. The experiment must be stopped as soon as the tested product is firm and hard.

First, the Petri dish is removed from the heating plate using crucible tongs. After 5 min, test the cooled product for strength. Alternatively, immediately pour the reaction product into a mold. The reaction product can also be compared with plastic samples, for example, pellets and filaments (Figure 6).

2.2.1. Observations

After the reactant have been combined with the catalysts, a steady gasification can be observed above the Petri dish. This steady gasification can still be observed after more than 20 minutes.

In the reaction mixture, a change from a clear liquid to a white turbidity in the liquid can be observed. In addition, the reaction mixture becomes more solid as it progresses. The reaction product can also be melted down as often as desired.

2.2.2 Results

Initially, the observed gasification is the water from the lactic acid solution. After about 5 to 10 minutes, however, this has evaporated completely. So, from then on, it is only water from the polycondensation reaction. The solidification indicates the formation of the polymer. Further indications for the formation of a thermoplastic, such as PLA, can be obtained by repeated melting and cooling. At the end of the experiment, polylactic acid is present (Figure 5).

Figure 5. Result of proposed student experiment

As polylactic acid is a thermoplastic, it can be melted down again and hardened as desired. The students can also compare the PLA they have synthesized with a purchased pellet (Figure 6). Although the two products are visually comparable, the purchased pellets shows better material properties (lower fragility) due to the purification of the product and the addition of additives.

Figure 6. Comparison of PLA synthesized in the experiment (left) with a purchased PLA pellet (right: Eolas Prints®)

Different tasks can support school students in their interpretation by leading them from the structural formula and the functional groups of lactic acid via polycondensation as a reaction type and the reaction product water to the reaction equation and the drawing of the monomer.

3. Summary and Outlook

The topic of plastics is a central component of many syllabi in different countries. The experiment on PLA synthesis presented here offers school students the possibility to independently synthesize a polymer as a base for plastics such as PLA. School students have already successfully conducted this experiment in the out-of-school laboratory "TüChemLab". This experiment has two aims: On the one hand, the school students should better understand the chemical reaction. Further analyzes should be carried out during the experiment so that the students can better understand the polycondensation that occurs. For example, students could qualitatively analyze the formation of water as a reaction product. In addition, the students could measure the increase in pH value as an indication of the decrease in lactic acid concentration. The analyzes enable the students to make well-founded statements about the course of the reaction and the formation of polylactic acid.

On the other hand, the reaction product should also be analyzed in more detail from a scientific perspective. For this purpose, FTIR spectroscopy can be used as a typical investigation method for polymers.

We aim to further develop this experiment in order to demonstrate the vital link between 3D printing and plastics. The students should process the polymer (composition) and produce a plastic. Thus, the chemical side of the starting material and the plastic as a printing filament should also be considered. In addition, models can be printed with PLA in chemistry lessons.

However, in terms of sustainability, it should be taken into account that 3D printing produces plastic waste (Figure 7).

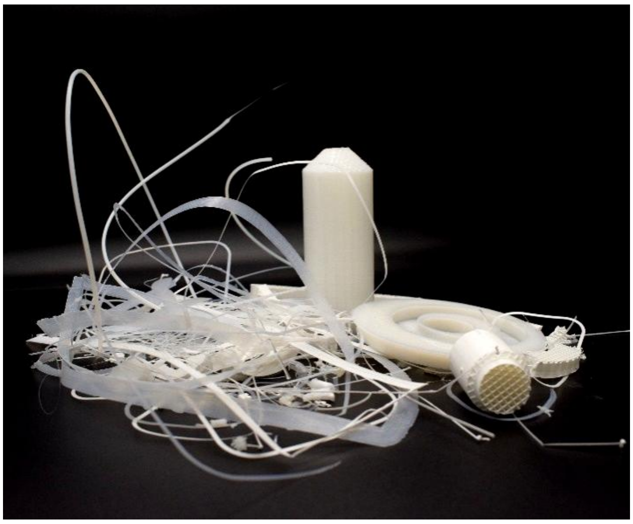

Figure 7. Plastic waste from 3D printing

This waste is an easily accessible example that can be used to integrate the topics of sustainability and circular economy into chemistry education. Currently, further efforts are being made in our research group to develop an experiment that allows the direct use of the printing waste to form a new PLA filament.

In addition, the cycle of plastics recycling shall be taken into account. How does plastic recycling take place in the industry? What opportunities does mechanical recycling offer? What are the difficulties? Are there ways to give practical access and experience? How can chemistry education support school students in their sustainable action?

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References

[1] Ministerium für Kultus, Jugend und Sport Baden-Württemberg, *Bildungsplan des Gymnasiums. Chemie – Überarbeitete Fassung vom 25. März 2022*, Neckar-Verlag, Stuttgart, 2022.

[2] Meier, M., Schubatzky, T., Obczovsky, M., Thoms, L.-J., and Thyssen, C., Fachdidaktische Perspektiven und Szenarien des 3D-Drucks im naturwissenschaftlichen Unterricht, *MNU Journal*, 75 (1), 2022, 79–84.

[3] Scheid, M., Hock, K. and Schwarzer, S., 3D Printing in Chemistry Teaching: From a Submicroscopic Molecule to Macroscopic Functions - Development of a Molecular Model Set and Experimental Analysis of the Filaments. *World Journal Chemistry Education*, 7 (2), 2019, 72–83.

[4] Schwarzer, S., Parchmann, I., Hübner, D., Wahler, J., Liesener, F., Pachaly, B. and Zdzieblo, J., Basisartikel: Strukturen nach Maß - Von der chemischen Forschungsidee zu Erkenntnissen und Produkten. *NiU Chemie*, 29 (164), 2018, 2–9.

[5] Paukstelis, P.J., MolPrint3D: Enhanced 3D Printing of Ball-and-Stick Molecular Models. *J. Chem. Educ.*, 95 (1), 2018, 169–172.

[6] Jones, O.A.H. and Spencer, M.J.S. A Simplified Method for the 3D Printing of Molecular Models for Chemical Education. *J. Chem. Educ.*, 95 (1), 2018, 88–96.

[7] Renner, M., und Griesbeck, A. (2020) Think and Print: 3D Printing of Chemical Experiments. *J. Chem. Educ.*, 97 (10), 3683–3689.

[8] Linkwitz, M., Zidny, R., Nida, S., Seeger, L., Belova, N. and Eilks, I., Simple green organic chemistry experiments with the kitchen microwave for high school chemistry classrooms. *Chem. Teach. Int.*, 4 (2), 2022, 165–172.

[9] Zowada, C., Linkwitz, M., Siol, A. and Eilks, I., Evaluating Sustainability in chemistry teaching. *CHEMKON*, 27 (8), 2020, 365–372.

[10] Vacano, B., Mangold, H., and Seitz, C., Kunststoffe im Kreislauf: Die Zeit ist reif. *Chem. Unserer Zeit*, 55 (6), 2021, 374–385.

[11] Sin, L.T. and Bee Soo Tueen, *Polylactic acid: a practical guide for the processing, manufacturing, and applications of PLA*, Elsevier, Oxford, United Kingdom; Cambridge, MA, United States, 2019.

[12] Masutani, K. and Kimura, Y., PLA Synesis. From the Monomer to the Polymer, in Jiménez, A., Peltzer, M. and Ruseckaite, R. (Eds.) *Polymer Chemistry Series*, Royal Society of Chemistry, Cambridge, 2014, 1–36.

[13] Taib, N.-A.A.B., Rahman, M.R., Huda, D., Kuok, K.K., Hamdan, S., Bakri, M.K.B., Julaihi, M.R.M.B. and Khan, A., A review on poly lactic acid (PLA) as a biodegradable polymer. *Polym. Bull.*, 80 (2), 2023, 1179–1213.

[14] Haider, T.P., Völker, C., Kramm, J., Landfester, K. and Wurm, F.R., Plastics of the Future? The Impact of Biodegradable Polymers on the Environment and on Society. *Angew. Chem. Int. Ed.*, 58 (1), 2019, 50–62.

[15] Wagner, G., Werkstoffe aus Milch und Zucker. Biologisch abbaubare Werkstoffe im Chemieunterricht. *NiU Chemie*, 10 (50), 1999, 24–28.

[16] Remus, L., PLA aus Milchsäure. Ein Kurzversuch für die Sek. I. *PdN Chemie*, 54 (4), 2005, 44–47.

[17] Robert, J.L. and Aubrecht, K.B., Ring-Opening Polymerization of Lactide To Form a Biodegradable Polymer. *J. Chem. Educ.*, 85 (2), 2008, 258–260.

[18] Linkwitz, M., and Eilks, I. (2020). Greening the Senior High School Chemistry Curriculum: An Action Research Initiative. In *ACS Symposium Series*, American Chemical Society, Washington, DC, 55–68.

[19] Jamshidian, M., Tehrany, E.A., Imran, M., Jacquot, M. and Desobry, S., Poly-Lactic Acid: Production, Applications, Nanocomposites, and Release Studies. *Compr. Rev. Food Sci. Food Saf.*, 9 (5), 2010, 552–571.