# Analysis of 3D printing possibilities for the development of practical applications in synthetic organic chemistry

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The possibility of rapid manufacturing of customized chemical labware and reactionware by three-dimensional (3D) printing is discussed. The advantages and disadvantages of this approach to the design of chemical equipment from different engineering plastics were demonstrated and the suitability of some materials for chemical applications was estimated: PP > PLA >ABS > PETG (PP is polypropylene, PLA is polylactide, ABS is acrylonitrile butadiene styrene, and PETG is polyethylene terephthalate glycol). The procedure described is a powerful tool for the production of both typical and unique chemical labware; to date, the fused deposition modeling (FDM) method is already available for the everyday use in chemical laboratories. The examples of successful application of 3D-printed products were demonstrated: solvent resistance and impermeability were assessed, as well as Pd(OAc)<sub>2</sub>-catalyzed crosscoupling between *p*-bromotoluene and phenylboronic acid and Ni(acac)<sub>2</sub>-catalyzed hydrothiolation of alkyne with thiophenol were performed.

Key words: 3D printing, FDM method, labware, cross-coupling, hydrothiolation.

Key features of chemical studies are a wide variety of reagents, products, and types of chemical reactions. A great number of chemical transformations has been discovered in the field of organic synthesis,<sup>1,2</sup> photochemistry,<sup>3</sup> catalysis,<sup>4</sup> materials science,<sup>5</sup> and biotechnology.<sup>6</sup> It is no wonder that chemical sciences need a great variety of labware to carry out chemical reactions. Many chemical processes require unique labware and equipment whose production from glass or metal by classical methods can be complex and expensive.

The manufacture, cleaning, reuse, and storage of glassware and laboratory equipment are often the most resource- and time-consuming steps of a chemical study. The emergence of a versatile technology for rapid production of labware can change dramatically the current situation.<sup>7</sup> Since the advent of three-dimensional (3D) printing, forecasts on revolutionary changes in practical implementation of chemical experiments have been being made.

The methodology of 3D printing assumes manufacturing of a product based on its three-dimensional model. Modern computer aided design systems possess necessary possibilities for the design of three-dimensional objects. Therefore, 3D printing minimizes the distance between a project and its realization. Having designed a three-dimensional model of a future product, one can start its automated manufacture with a selected material.

Application of a single-use labware (no cleaning and storage) will simplify and make cheaper chemical synthe-

sis. On the one hand, 3D printing allows production of single-type labware, such as test tubes, flasks, beakers, cuvettes, *etc.* About one hundred and more (depending on the size) such products can be produced in one workday. On the other hand, 3D printing allows one to considerably accelerate and make cheaper the production of a complex chemical reactors with unique construction whose manufacture by other methods is either very complex or unreasonably expensive. Thus, chemists cease to be restricted in their work only with commercial labware and can create its by themselves customizing the labware to the features of certain experiment.<sup>8</sup>

Many researchers wonder whether 3D printing will indeed introduce a new dimension into laboratory chemical applications.

In the present work, the most common and available 3D printing process, Fused Deposition Modeling (FDM), was tested for practical chemical studies. Virtually any thermoplastic polymer is suitable for this process and, to date, a relatively wide range of inexpensive materials are available, which allows one to select a material being the most suitable for certain chemical task. In addition, FDM 3D printers have a simple design, are easy-to-handle and the cheapest devices for 3D printing. We tested the most widely used plastics for FDM printing: PLA (polylactide), ABS (acrylonitrile butadiene styrene), PETG (polyethylene terephthalate glycol), and PP (polypropylene).

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The most important reactions for the carbon—carbon and carbon—heteroatom bond formation, in particular, the Suzuki—Miyaura cross-coupling catalyzed by palladium acetate  $Pd(OAc)_2$  and alkyne hydrothiolation catalyzed by nickel acetylacetonate (Ni(acac)<sub>2</sub>), were performed in an FDM plastic labware. These chemical transformations are a powerfool tool for the preparation of complex organic substances with atomic precision.<sup>1,2</sup>

## **Results and Discussion**

**3D printing technology.** Three-dimensional printing is based on the additive principle. In the FDM printing process, a material as a thin filament (with a typical diameter of 1.75 or 3.00 mm) reeled on a spool is fed into an extruder, where it is heated to specified temperature. A thermoplastic polymer passes into a viscous-flow state and is extruded from a nozzle as a thin wire. The extruder is moved over a platform where a model is built layer-by-layer. In such a way, we created a typical chemical labware (Figs 1 and 2) to carry out this work. The layer height defines to a some degree the spatial printing resolution: the lower is the layer height, the smaller are the parts that can be reproduced in a printed product. For example, even a relatively high layer height (0.2 mm) allows creating a large operable thread to screw on tube caps and to provide a test tube with tightness during the experiment (see Fig. 2, b, c).

Thus, our experiment showed that 3D printing is a simple and convenient method for application in the everyday practice of a chemical laboratory. The next aim of our work was to study whether the FDM-created labware is suitable for chemical experiment. To test the stability of plastics under the synthesis conditions and to perform chemical reactions, we chose the test tubes as the most widespread, simple, and convenient type of labware used in the vast majority of chemical laboratories (see Fig. 2). To produce test tubes by FDM, four different materials were used: ABS, PETG, PLA, and PP (see Fig. 2). Cross-coupling and hydrothiolation were performed in test tubes with screw caps which were equipped with a septum for better tightness (see Fig. 2, *b*, *c*).

To evaluate the suitability of 3D-printed labware, three types of tests were performed: a) evaluation of chemical resistance to solvents; b) pressure and vacuum leak tests; and c) stability in chemical reactions.

**Chemical resistance of the FDM-printed labware.** The present work shows the effect of chemical solvents under conditions of a chemical experiment on the labware produced by the FDM process. For this purpose, screw-capped test tubes made of ABS, PLA, PP, and PETG plastics were printed (see Fig. 2).

The test tubes were filled with solvents which were stirred for 1 h at  $\sim 20$  or 50 °C. The solvent was then transferred into a flask and evaporated. The flask was weighed; the weight gain showed the amount of the plastic material extracted by a solvent. The intensity of solvent interaction with a platic material serves as a suitability index of the material for chemical experiments in different media (Table 1).

The data given in Table 1 suggest that, in this series, there is no universal thermoplastic material which would be stable in all solvents. At ~20 °C, ABS test tubes were dissolved in the most of organic solvents (acetone, MeCN,  $CH_2Cl_2$ , and THF) and, at 50 °C, the test tube walls became



Fig. 1. Examples of typically used labware produced by FDM 3D printing with PLA: Erlenmeyer flask, round-bottom flask, funnel, test tubes, and beaker.

Note. Figures 1 and 2 are available in full color on the web page of the journal (http://www.link.springer.com).



**Fig. 2.** Different types of test tubes used in the cross-coupling experiments: short test tubes with threadless caps (a); 3D-printed thread on the external side of a tube and inside a cap (b); and elongated screw-capped tubes made of different materials (c).

softer in DMSO and toluene. Water, hexane, diethyl ether, and ethanol do not dissolve plastic materials and, therefore, are considered as mild solvents: these solvents are suitable for reactions in test tubes made of any tested material (ABS, PETG, PLA, and PP).

Table 1. Solvent resitance<sup>a</sup> of plastic test tubes (50 °C, 1 h)

| Solvent                      | ABS | PLA | РР | PETG    |
|------------------------------|-----|-----|----|---------|
| Acetone                      | b   | ±   | ±  | +       |
| Acetonitrile (MeCN)          | _b  | _   | +  | +c      |
| Water                        | +   | +   | +  | $+^{c}$ |
| Hexane                       | +   | +   | ±  | $+^{c}$ |
| Dimethylsulfoxide (DMSO)     | _   | ±   | +  | _       |
| Dichloromethane $(CH_2Cl_2)$ | _b  | _   | ±  | _       |
| Diethyl ether <sup>c</sup>   | +   | +   | +  | $+^{c}$ |
| Tetrahydrofuran (THF)        | b   | _   | ±  | _       |
| Toluene                      | _   | ±   | ±  | ±       |
| Ethanol (EtOH)               | +   | +   | +  | +       |

<sup>*a*</sup> The plastic material is not suitable for solvent experiments (–); partially suitable: 2-7 mg of the plastic dissolved during the experiment (±); and chemically stable: the solvent has no effect on the plastic (+).

<sup>*b*</sup> ~20 °C, 1 h.

<sup>c</sup> The solvent partially permeates through the tube walls.

PLA test tubes dissolved in dichloromethane and THF and, during the experiment with acetonitrile at 50 °C, they lost rigidity and broke down. At room temperature, this effect was not so noticeable and test tubes did not lose their physical properties; therefore, PLA labware can be applied with MeCN without heating.

PETG test tubes dissolved only in dichloromethane and THF; however, another problem emerged during the study: the solvent permeated through the tube walls. This phenomenon is due to a specificity of the FDM three-dimensional printing process: PETG filaments upon printing were stacked above each other in layers and, apparently, do not stick together sufficiently to form a monolithic wall under printing parameters recommended for this material. As a result, the resulting product is porous and the solvent flows out of micropores.

PP test tubes showed the best chemical resistance to tested solvents. However, this material also has disadvantages, such as shrinkage during printing and necessity for their further mechanical processing to provide the accuracy in size. After additional mechanical processing, products contain fine polypropylene particles adhering to the product walls, which are sometimes difficult to remove completely.

**Impermeability of the FDM labware.** One of the most important properties of any chemical equipment defining

its suitability for everyday chemical experiments is its leaktightness. Therefore, the leak-tightness of printed test tubes was studied under excessive pressure of 1 bar produced by an air compressor and under reduced pressure of 30 mbar produced by a rotary evaporator (to examine how test tubes can keep vacuum during evaporation of a solvent). The PETG labware were found to be nontight in both cases, whereas the ABS, PLA, and PP products demonstrated a high tightness in all experiments.

It was found that not only the material type and the wall thickness of an product, but also its shape have effect on the labware tightness. In particular, 50-mL round-bottom polypropylene and PETG flasks were not leaktight in both vacuum and excessive pressure experiments. The leakage of flasks was first of all due to a high porosity of a material near its spherical bottom and in the fixation region of the flask neck, whereas, in the equatorial part of the flask, the material is sufficiently impermeable.

The reason for the leakage of all items is their layered structure. To dispose of this disadvantage, the material was fritted upon thermal postprocessing. However, heating of round-bottom polypropylene flasks at 200 °C resulted in an incomplete disappearance of microporosity and the flask remained permeable.

Thus, the best tightness parameters were observed for cylinder-shaped items made of ABS and PLA.

**Chemical reactions in the FDM labware.** At the next step of this study, we applied the printed test tubes in chemical synthesis. Suzuki-Miyaura cross-coupling was chosen as the model reaction (Scheme 1), since it proceeds under aerobic conditions in the water-alcohol medium and palladium nanoparticles act as the catalyst. To obtain reliable data, this reaction should be carried out in a labware containing no metal even in trace amounts, for that reason the labware should be cleared thoroughly after each exploitation or applied only ones,<sup>9</sup> that became possible upon introduction of the 3D printing technology into a laboratory practice. The reaction was performed in screw-capped glass, ABS, PP, PETG, and PLA test tubes (see Fig. 2, *b*, *c*).



Scheme 1



The reaction was carried out under heating in a heat block with a magnetic stirrer for 5 h. The visual control of the reaction was complicated, since only PETG test tubes

**Table 2.** Conversion of *p*-bromotoluene and product yield in the Suzuki—Miyaura reaction (see Scheme 1)

| Material | Conversion | Yield |  |  |
|----------|------------|-------|--|--|
|          | %          | %     |  |  |
| Glass    | 96         | 79    |  |  |
| ABS      | 94         | 54    |  |  |
| PETG     | 94         | 53    |  |  |
| PLA      | 95         | 50    |  |  |
| PP       | 93         | 42    |  |  |

are partially transparent, while tubes made of other plastics are nontransparent. After the reaction was completed, 50 µL of the reaction mixture was sampled into an NMR tube with CDCl<sub>3</sub>. The measured degree of conversion in all cases was >90%, but the product yield was the highest in glass test tubes (79%) and considerably exceeded the value obtained in plastic test tubes (42–54%, Table 2). The GC-MS study of the reaction mixture showed that, in plastic test tubes, p-bromotoluene was almost absent in solution, while triphenylboroxine was present in a considerable amount. It is most likely that this is due to the sorption activity of plastic materials towards *p*-bromotoluene, which caused a decrease in the product yield. When planning experiments in plastic labware, this phenomenon should be taken into account and its effect can be decreased using the excess of sorbing agent. It should be noted that the reaction mixture after completion of the reaction in the PP test tube virtually did not contain palladium particles: the catalyst was adsorbed on the tube walls.

The second model reaction was hydrothiolation of alkynes<sup>10</sup> with Ni(acac)<sub>2</sub> as the catalyst (Scheme 2). This reaction was performed in the medium being more aggressive towards plastic materials, toluene; therefore, ABS was not suitable for this reaction: the reaction mass due to partial dissolution of the plastic material was a thick and sticky mixture and we failed to extract the reaction product with petroleum ether.

#### Scheme 2



*i*. Ni(acac)<sub>2</sub> (2 mol.%), toluene, 40 °C, 3 h.

An interesting result was obtained during the experiment in a PLA test tube: the reaction mass contained an amorphous coarse precipitate which was easy to remove by filtration; that significantly facilitated the work up procedure.

**Table 3.** Conversion of thiophenol andproduct yield in hydrothiolation of alkynes(see Scheme 2)

| Material | Conversion | Yield |  |  |  |
|----------|------------|-------|--|--|--|
|          | %          | %     |  |  |  |
| Glass    | 68         | 47    |  |  |  |
| ABS      | *          | _     |  |  |  |
| PETG     | 71         | 27    |  |  |  |
| PLA      | 82         | 37    |  |  |  |
| PP       | 82         | 44    |  |  |  |

\* ABS dissolves in toluene.

The degrees of conversion for the reactions in test tubes are also related to sorption of reagents by plastics (Table 3). However, this effect was decreased due to the use of two-fold excess of thiophenol and the product yield, for example, in the PP test tube, differed insignificantly from that obtained in the glass tube.

#### \* \* \*

Three-dimensional printing technology can find a wide application in chemical laboratory and become a versatile tool for the design of not only standard labware (test tubes, flasks), but also a more complex unique equipment. This possibility allows solving unconventional problems which earlier required high time and material costs. This work was aimed at the study of the applicability of a labware produced by fused deposition modeling (FDM) in order to reveal possible operational difficulties and to take them into account in the future. The test tubes used in the present work are only a convenient "form" to test materials commonly used for FDM 3D printing.

We showed that all plastic materials under study are suitable for application in water-alcohol media; therefore, the 3D printing technology can find a wide application in biology and medicine, especially, in the case when a single-use small-size labware, such as arrays of cuvettes, vials, weighing bottles, etc, is needed. In more aggressive media, one should use materials with a high chemical resistance (PP). In the case when a thermoplastic material was stable under the reaction conditions, the data obtained were virtually no different from those obtained in the glass. It should be noted also that such materials as PLA and ABS are more suitable for 3D printing, since the obtained model possesses a higher dimensional accuracy and integrity and requires minimum mechanical postprocessing, whereas PP shrinks considerably, which results in the difference between the sizes of a printed product and its computer model.

As it follows from the overall assessment (Table 4), polypropylene is the most suitable material for chemical experiments due to the highest resistance to chemical reagents; PLA possesses lower chemical resistance, however

 Table 4. Overall test of the suitability of FDM labware for chemical experiments

| Method of use                               | РР   | PLA  | ABS               | PETG              |
|---|------|------|-------------------|-------------------|
| Mild solvents <sup>a</sup>                  | +    | +    | +                 | ±                 |
| Agressive solvents <sup>b</sup>             | +    | _    | _                 | _                 |
| Pressure/vacuum                             | ±    | +    | +                 | _                 |
| Chemical reactions<br>in mild solvents      | +    | +    | +                 | +                 |
| Chemical reactions<br>in agressive solvents | +    | +    | -                 | ±                 |
| General score                               | Good | Good | Satis-<br>factory | Satis-<br>factory |

<sup>a</sup> Mild solvents are Et<sub>2</sub>O, EtOH, hexane, and H<sub>2</sub>O.

<sup>b</sup> Agressive solvents are acetone, MeCN, CH<sub>2</sub>Cl<sub>2</sub>, THF, toluene, and DMSO.

PLA labware are characterized by better properties: they have almost no pores and are tight, the material does not shrink considerably and is convenient for additional mechanical postprocessing. Although PETG items are partially transparent and this fact is their doubtless advantage; the layered structure obtained upon printing hinders the application of PETG-printed labware due its high porosity. The low chemical resistance of ABS considerably restricts its applicability in chemistry. As a result, one can conclude that PP and PLA are much more suitable for printing a labware compared to ABS or PETG. A general order of the functionality of plastic materials for chemical applications is as follows: PP > PLA > ABS > PETG.

For further development, the following disadvantages use of FDM-printed labware should be noted:

• the plastic labware is not transparent, which makes it difficult to control visually the course of the reaction;

• some items, in particular, PETG and PP ones, are not tight and a solvent permeates through the material layers;

• the data on the chemical stability of materials available for 3D printing are limited; therefore, the effect of reagents on materials should be checked prior to experiment;

• even if a material itself do not decompose on exposure to a chemical reagent, during the experiment one can find that the reagent escapes from the reaction due to a high sorption capacity of the plastic material;

• sometimes there emerge difficulties upon stirring the reaction mixture, since even at insignificant softening of the material, the magnetic stir bar sticks in the plastic and stops to fulfil its function;

• the properties of a plastic material of the same type can differ noticeably depending on the manufacturer; therefore, in each case one should test the material in several model experiments.

Beyond all doubt, a rapid development of the 3D printing technology occurring in the present time will provide its considerable improvement and, in the nearest future, one can expect an extensive use of a unique customized labware made of not only plastics, but also of metal alloys and even glass in chemical studies.<sup>11</sup>

# **Experimental**

PLA and ABS (ESUN), as well as PETG and PP (FL-33) were used as plastic materials.

**3D** Printing. All labware items were produced by fused deposition modeling (FDM) using a Picaso 3D Designer Pro 250 printer. The diameter of the starting plastic filament in all cases was equal to 1.75 mm, the layer height (resolution along the Z axis) was 0.2 mm, the extrusion multiplier was 0.9-1.0, the printing speed was 45 mm s<sup>-1</sup>, and the infill was 100%.

For the PLA plastic, the extruder temperature ( $T_e$ ) was 210 °C, the table temperature ( $T_t$ ) was 50 °C; during printing cooling was performed using a fan installed on the printer extruder. For ABS,  $T_e = 230$  °C and  $T_t = 100$  °C. For PETG,  $T_e = 210$  °C and  $T_t = 50$  °C. For PP,  $T_e = 240$  °C and  $T_t = 90$  °C and no cooling was used. The total time of printing all items showed in Fig. 1 was ~9 h.

Printing parameters were set and the G code was generated using the Repetier-Host 1.5.6 program package.<sup>12</sup>

Solvent resistance test of labware. A solvent (3 mL) was placed in plastic test tubes and stirred for 1 h at ~20 or 50 °C. The whole solvent was poured into a flask and evaporated. As a result, in the cases when the plastic material was dissolved, after evaporation of the solvent a dry residue remained and its weight was measured.

Leakage test of labware. A) Excessive pressure of 1 bar. Plastic test tubes or flasks were connected to an air compressor and immersed in water. The excessive pressure produced by the compressor was set at the value of 1 bar. The appearance of air bubbles after switching on the compressor allowed to determine the location of pores. B) Vacuuming of test tubes. Plastic tubes were connected to a rotary evaporator to produce a reduced pressure of 20-30 mbar. The test tube was considered to be leak-tight if the readings of a vacuum meter did not change for 15 min.

**Cross-coupling.** 4-Bromotoluene (0.5 mmol, 0.086 g) was added to a solution of phenylboronic acid (0.6 mmol, 0.073 g), Et<sub>3</sub>N (1 mmol, 0.101 g), and Pd(OAc)<sub>2</sub> (0.01 mmol, 0.002 g) in EtOH (1 mL). The reaction was performed for 5 h at 40 °C. The precipitate was separated by centrifugation and the organic phase was collected using a Pasteur pipette. The precipitate was washed additionally with ethanol ( $2 \times 1.5$  mL). The solvent was evaporated. The product yield was calculated from the <sup>1</sup>H NMR spectrum using trimethyl(phenyl)silane as the internal standard.

**Hydrothiolation.** The reaction was performed according to a known procedure<sup>13</sup> using toluene as the solvent. A solution of 2-methyl-3-butyn-2-ol (1 mmol, 0.084 g) and Ni(acac)<sub>2</sub> (0.02 mmol, 0.005 g) in toluene (0.4 mL) was cooled with stirring to 10 °C. Thiophenol (2 mmol, 0.220 g) was added and the test tube was purged with argon and closed. The reaction was performed at 40 °C for 3 h. The reaction mass was filtered through zeolite to separate the catalyst and the unreacted starting reagents were removed *in vacuo*.

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