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# Instability of thermoplastics as a key feature in catalyst preparation

**Kirill S. Erokhin,**[*a] **Manuk A. Kartashian**[a,b] **and Nina M. Ivanova**[a]

[a] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: erokhin@ioc.ac.ru*
[b] *D. I. Mendeleev University of Chemical Technology of Russia, 125047 Moscow, Russian Federation*

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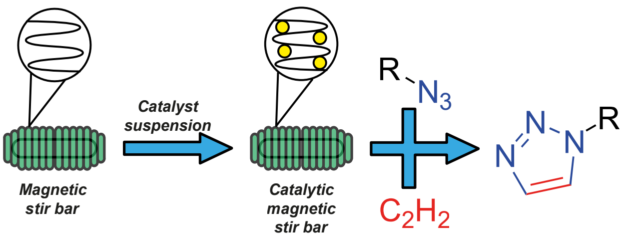
**The feasibility of fabricating catalytically active structures based on thermoplastic polylactide, polyethylene terephthalate glycol (PETG) and acrylonitrile–butadiene–styrene using 3D printing of sleeves for magnetic stir bars was investigated. It was shown that the correct selection of solvents for thermoplastic modification and reaction performance plays a key role. PETG-based catalytic stir bars demonstrated the best efficiency and recyclability in the azide–alkyne cycloaddition reaction and allowed to synthesize a variety of triazoles from acetylene.**



*Keywords*: additive manufacturing, fused filament fabrication, 3D printing, thermoplastic, azide–alkyne cycloaddition, acetylene.

Catalysis is one of the most important areas in the chemical industry. Catalysts facilitate transformations in both petrochemistry and fine organic synthesis.[1–3] The key area of modern catalysis is shaping catalysts for use in chemical reactors.[4]

Additive technologies have reached a new milestone in the development of science and industry.[5] They make it possible to manufacture products of various shapes and provide rapid prototyping. 3D printing has applications in biology,[6] medicine,[7] pharmaceutics,[8] building,[9] engineering[10] and other fields. In chemistry, they simplify the production of reactors with intricate internal structures, thereby enhancing the convenience and efficiency of chemical processes.[11–13] 3D printing was also used in the development of catalysts.[14–16] Thus, printing by the Direct Ink Writing method with $Al_2O_3/Cu(NO_3)_2$ ink made it possible to prepare catalysts for the Ullmann reaction.[17] Adding *p*-TsOH to a photopolymer resin enables the production of catalytic mixers for the Mannich reaction using stereolithography.[18]

One of the most accessible and widespread methods of 3D printing is Fused Filament Fabrication (FFF). In this process, a filament of thermoplastic material passes through a heated nozzle where it melts to become viscous. The molten plastic is then extruded onto the surface of the table and hardens as it cools. Despite its popularity, this printing method has very limited application in organic synthesis. The reason for this is the low resistance of polymer materials to organic solvents. We have previously demonstrated that printed products can swell and dissolve when exposed to solvents.[19] However, the fact that a material is unstable in one solvent but stable in another can form the basis for the development of catalytic structures. This work demonstrates a high potential for producing azide–alkyne cycloaddition catalysts using the most common materials in FFF 3D printing: polylactide (PLA), acrylonitrile–butadiene–styrene (ABS) and polyethylene terephthalate glycol (PETG).

In the first stage, sleeves for magnetic stir bars were manufactured using FFF 3D printing. The sleeves were made in the form of capsule halves with an outer diameter of 5.6 mm and an inner diameter of 3.6 mm [Figure 1(*a*)]. The magnetic stir bar was placed inside the capsule and fixed tightly. The sleeves were made of PLA, ABS and PETG [Figure 1(*b*)]. Previous studies have shown that these materials exhibit moderate resistance to DMF.[19] This solvent was chosen to modify the materials. A study was conducted on the swelling of the materials in DMF, which was assessed by the change in mass after immersion in the solvent for one hour. The mass change for PETG was 38 ± 8%, while for PLA it was slightly lower (31 ± 4%). Exposure of the ABS sleeve to DMF for the experimental time resulted in a loss of its shape. The azide–alkyne cycloaddition with acetylene in dimethyl sulfoxide (DMSO) was chosen as a model reaction.[20] The study of the behavior of the materials in DMSO showed that a mass gain was observed for both PLA (18 ± 2%) and PETG (12 ± 2%), but the mass gain was smaller for PETG. Thus, PETG is more resistant to DMSO and less resistant to DMF, which makes it a suitable candidate for manufacturing catalytic structures by impregnation. After the experiments, the solutions were analyzed by HRMS-ESI to evaluate the leaching of the material (Figures S1–S4, see Online Supplementary Materials). In the case of PLA, oligomer peaks are observed in the mass spectra of both DMF and DMSO. In the case of PETG in DMF, oligomer peaks are also observed, indicating partial dissolution. In contrast, no PETG oligomer peaks were detected in DMSO, confirming its resistance to this solvent.

In the next stage, the stir bars were modified using CuI as a catalytic additive. For this, the stir bars with 3D printed sleeves were immersed in a suspension of CuI in DMF for one hour at room temperature [Figure 1(*c*)]. The resulting catalytic structures

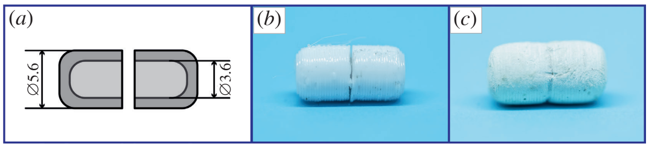
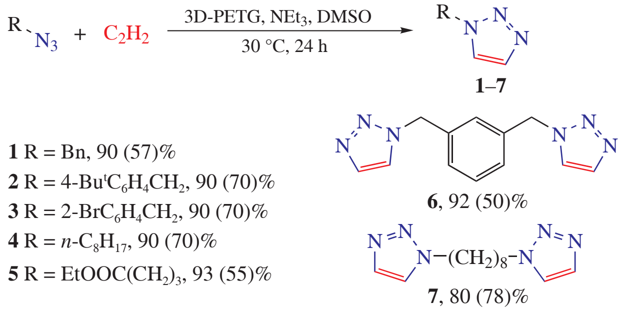


**Figure 1** 3D printed sleeve for magnetic stir bar: (*a*) design, (*b*) view of the sleeve printed from PETG and (*c*) view of the PETG sleeve after immersion in CuI solution in DMF.



**Scheme 1**

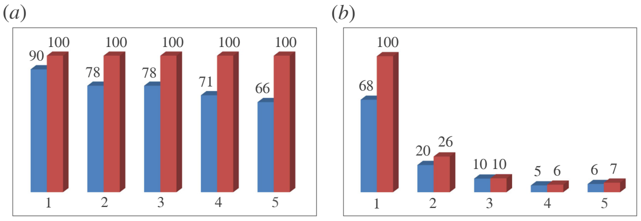


**Figure 2** Recycling of prepared catalysts 3D printed with (*a*) PETG and (*b*) PLA in the [3+2]-cycloaddition reaction of benzyl azide with acetylene.[†] Blue and red bars correspond to the NMR yield and conversion, respectively.

were evaluated in the azide–alkyne cycloaddition reaction with acetylene (Scheme 1).

Recycling of the obtained catalysts showed that in the case of PETG, the activity is maintained for three cycles, after which it begins to slowly decrease. In all cases, 100% conversion was observed [Figure 2(*a*)]. This suggests that either the initial benzyl azide or the resulting product is adsorbed on the surface of the material. To analyze the probability of reagent adsorption on the stir bar surface, the sleeves were dissolved in methylene chloride after the 1st and 2nd reaction cycles. GC-MS analysis of the resulting solution showed the presence of benzyltriazole **1** (Figures S5 and S6). Thus, adsorption of the product on the stir bar material is observed. This explains the lower yield compared to conversion. However, in the case of PLA, a critical decrease in yield is observed already in the 2nd cycle [Figure 2(*b*)]. A study of the sleeve surface morphology using scanning electron microscopy (SEM) showed that immersion of PETG stir bars in a CuI/DMF suspension leads to smoothing of the layers and partial dissolution of the material (Figure 3). As a result, the surface morphology becomes quite pronounced with pores and cavities forming in the material. In the case of PLA, the morphology changes to a lesser extent, the layered structure is preserved, while traces of material leaching are also present (Figure 4). EDX analysis of the sleeve surface after modification revealed CuI particles on the surface (Figures S7 and S9), whereas no Cu or I was observed on the PLA surface after the 1st reaction cycle (Figure S8). In contrast, Cu and I remain on the PETG surface, although in smaller amounts (Figure S10). Thus, CuI is almost completely leached from the PLA surface in one cycle, whereas in the case of PETG, CuI leaching is less pronounced. Catalyst leaching from the PETG surface into solution is also confirmed by the presence of ions in the reaction solution, detected by HRMS-ESI, the isotopic distribution of which corresponds to Cu-containing compounds (Figures S11 and S13). In addition, EDX analysis of the reaction mixtures after removing the stir bar and evaporating the solvent revealed the presence of Cu and I (Figures S12 and S14). Thus, the occurrence of homogeneous catalysis, caused by leaching and dissolution of copper salt, is most probable.

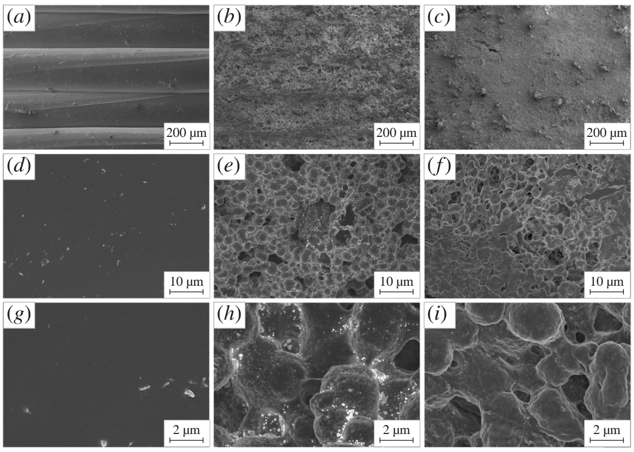


**Figure 3** SEM images of PETG sleeves at different magnifications: (*a*),(*d*),(*g*) initial state; (*b*),(*e*),(*h*) after immersion in CuI/DMF suspension; (*c*),(*f*),(*i*) after use for the benzyl azide cycloaddition reaction.

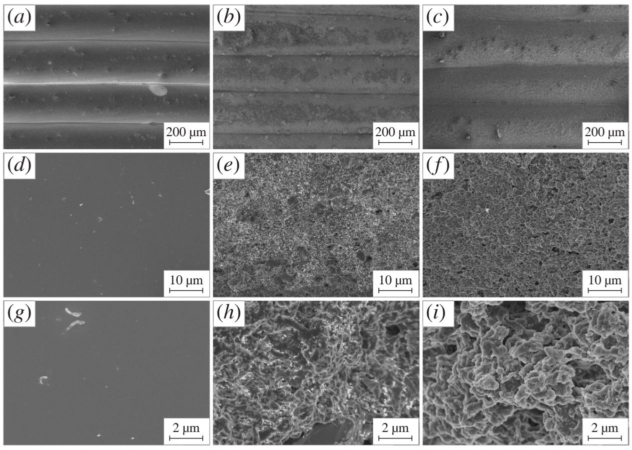


**Figure 4** SEM images of PLA sleeves at different magnifications: (*a*),(*d*),(*g*) initial state; (*b*),(*e*),(*h*) after immersion in CuI/DMF suspension; (*c*),(*f*),(*i*) after use for the benzyl azide cycloaddition reaction.

To understand the scope and limitations of the obtained 3D printed CuI/PETG stir bar as a catalyst, a series of substrates were tested in the azide–alkyne cycloaddition reaction involving acetylene (see Scheme 1; yields of isolated products are given in parentheses). The target triazoles **1**–**5** were obtained in good yields. Good yields were also observed for bistriazoles **6** and **7**. Experimental data and characterization of triazoles **1**–**7** are provided in Online Supplementary Materials. In addition, product **2** was characterized by X-ray diffraction analysis (Figure 5).[†]

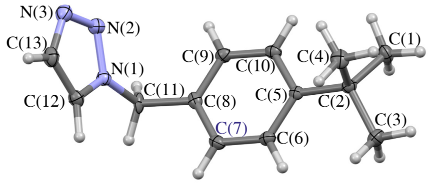


**Figure 5** Molecular structure of compound **2** in crystal with non-hydrogen atoms represented by displacement ellipsoids ($p$ = 50%).

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[†] Reaction conditions: $BnN_3$ (0.5 mmol), triethylamine (0.2 mmol), DMSO presaturated with $C_2H_2$ (1 ml), 30 °C, 24 h.

[†] *Crystal data for* **2**. $C_{13}H_{17}N_3$, $M$ = 215.29, orthorhombic, space group $Pca2_1$, copper radiation ($\lambda$ = 1.54184 Å), at 100 K: $a$ = 20.18697(13), $b$ = 5.78964(3) and $c$ = 20.16168(12) Å, $V$ = 2356.40(2) Å$^3$, $Z$ = 8, $d_{calc}$ = 1.214 g cm$^{-3}$, $\mu$ = 0.577 mm$^{-1}$, $F(000)$ = 928. Total of 28053 reflections were measured and 5066 independent reflections ($R_{int}$ = 0.0320) were used. The refinement converged to $wR_2$ = 0.0912 and GOF = 1.057 for all independent reflections [$R_1$ = 0.0338 was calculated for 5001 observed reflections with $I > 2\sigma(I)$].

CCDC 2444362 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk.

Thus, it was demonstrated that the selection of an appropriate pair of solvents for modification and reaction allows obtaining catalytic structures 3D printed from thermoplastic materials. In the first solvent, the material should exhibit moderate stability. In the second solvent, the material should be stable. In this work, PETG-based catalytic stir bars were developed, which showed efficiency in the azide–alkyne cycloaddition reaction with acetylene, giving the target triazoles in moderate to high yields. The thermoplastic-based catalyst operates in a catalyst cocktail mode initiated by leaching.[21,22] The catalytic stir bar can be recycled at least three times, which makes it suitable for use in organic synthesis. This work demonstrates the high potential of soluble thermoplastics as carriers of catalytically active species. Low resistance of thermoplastic to solvents can be used as a powerful tool in the field of catalyst preparation.

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*Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7811.

## References

1 S. A. Yakukhnov, E. O. Pentsak, K. I. Galkin, R. M. Mironenko, V. A. Drozdov, V. A. Likholobov and V. P. Ananikov, *ChemCatChem*, 2018, **10**, 1869; https://doi.org/10.1002/cctc.201700738.

2 R. M. Mironenko, E. R. Saybulina, M. V. Trenikhin, R. R. Izmailov, K. A. Lotsman, K. S. Rodygin and V. P. Ananikov, *ChemCatChem*, 2021, **13**, 3656; https://doi.org/10.1002/cctc.202100631.

3 I. S. Mashkovsky, P. V. Markov, A. V. Rassolov, E. D. Patil and A. Yu. Stakheev, *Russ. Chem. Rev.*, 2023, **92**, RCR5087; https://doi.org/10.59761/rcr5087.

4 V. G. Baldovino-Medrano, C. Alcázar, M. T. Colomer, R. Moreno and E. M. Gaigneaux, *Appl. Catal., A*, 2013, **468**, 190; https://doi.org/10.1016/j.apcata.2013.08.041.

5 A. A. Potapov, V. M. Volgin, A. P. Malakho and I. V. Gnidina, *Russ. Chem. Rev.*, 2024, **93**, RCR5127; https://doi.org/10.59761/rcr5127.

6 C. M. B. Ho, A. Mishra, K. Hu, J. An, Y.-J. Kim and Y.-J. Yoon, *ACS Biomater. Sci. Eng.*, 2017, **3**, 2198; https://doi.org/10.1021/acsbiomaterials.7b00438.

7 M. E. Prendergast and J. A. Burdick, *Adv. Mater.*, 2020, **32**, 1902516; https://doi.org/10.1002/adma.201902516.

8 J. Goole and K. Amighi, *Int. J. Pharm.*, 2016, **499**, 376; https://doi.org/10.1016/j.ijpharm.2015.12.071.

9 D. Lowke, E. Dini, A. Perrot, D. Weger, C. Gehlen and B. Dillenburger, *Cem. Concr. Res.*, 2018, **112**, 50; https://doi.org/10.1016/j.cemconres.2018.05.018.

10 M. Grajewski, M. Hermann, R. D. Oleschuk, E. Verpoorte and G. IJ. Salentijn, *Anal. Chim. Acta*, 2021, **1166**, 338332; https://doi.org/10.1016/j.aca.2021.338332.

11 E. G. Gordeev and V. P. Ananikov, *Russ. Chem. Rev.*, 2020, **89**, 1507; https://doi.org/10.1070/rcr4980.

12 K. S. Erokhin and V. P. Ananikov, *Org. Process Res. Dev.*, 2023, **27**, 1144; https://doi.org/10.1021/acs.oprd.3c00112.

13 V. A. Korabelnikova, Y. V. Gyrdymova, E. G. Gordeev, A. N. Potorochenko, K. S. Rodygin and V. P. Ananikov, *React. Chem. Eng.*, 2025, **10**, Advance Article; https://doi.org/10.1039/d4re00249k.

14 C. H. Hornung, X. Nguyen, A. Carafa, J. Gardiner, A. Urban, D. Fraser, M. D. Horne, D. R. Gunasegaram and J. Tsanaktsidis, *Org. Process Res. Dev.*, 2017, **21**, 1311; https://doi.org/10.1021/acs.oprd.7b00180.

15 E. Bulatov, E. Lahtinen, L. Kivijärvi, E. Hey-Hawkins and M. Haukka, *ChemCatChem*, 2020, **12**, 4831; https://doi.org/10.1002/cctc.202000806.

16 J. Zhu, P. Wu, Y. Chao, J. Yu, W. Zhu, Z. Liu and C. Xu, *Chem. Eng. J.*, 2022, **433**, 134341; https://doi.org/10.1016/j.cej.2021.134341.

17 C. R. Tubío, J. Azuaje, L. Escalante, A. Coelho, F. Guitián, E. Sotelo and A. Gil, *J. Catal.*, 2016, **334**, 110; https://doi.org/10.1016/j.jcat.2015.11.019.

18 M. R. Penny and S. T. Hilton, *React. Chem. Eng.*, 2020, **5**, 853; https://doi.org/10.1039/C9RE00492K.

19 K. S. Erokhin, E. G. Gordeev and V. P. Ananikov, *Sci. Rep.*, 2019, **9**, 20177; https://doi.org/10.1038/s41598-019-56350-w.

20 L.-Y. Wu, Y.-X. Xie, Z.-S. Chen, Y.-N. Niu and Y.-M. Liang, *Synlett*, 2009, 1453; https://doi.org/10.1055/s-0029-1216745.

21 E. E. Ondar, J. V. Burykina and V. P. Ananikov, *Catal. Sci. Technol.*, 2022, **12**, 1173; https://doi.org/10.1039/D1CY02006D.

22 D. B. Eremin and V. P. Ananikov, *Coord. Chem. Rev.*, 2017, **346**, 2; https://doi.org/10.1016/j.ccr.2016.12.021.

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