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Compositions Based on Microporous Coordination Polymers for the Formation of Arbitrarily Shaped 3D Objects

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Abstract—A composition was proposed based on microporous coordination polymers curable upon evaporation of the liquid phase or upon component polymerization induced by UV irradiation, which allows fabrication of items of arbitrary configuration. The obtained 3D objects were shown to be, in principle, applicable as stationary phases for the separation of amine-based dyes by liquid chromatography.

Keywords: porous coordination polymers, curable composition, 3D objects, chromatography
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INTRODUCTION

The development and advancement of 3D printing technique brought about revolutionary changes in the views on the fabrication of items for diverse areas of human activity: parts of sophisticated machines, buildings, elements of microelectronic devices, medical implants and so on [1–4]. The items that were traditionally manufactured using special complex equipment can be literally printed using a universal 3D printer [5, 6].

By 3D printing is meant the process of fabrication of a physical object on the basis of its digital 3D model, which is usually accomplished by successive deposition of thin layers of a material [7]. 3D printing can be implemented in manual devices, for example, a 3D pen called 3Doodler was recently developed [8]. The benefit of 3D printing is the possibility of automated fabrication of articles of any configuration. The size of article is determined by characteristics of the printer, while the minimum size of an article part is determined by both characteristics of the printer and characteristics of the printing material, ink, which is below referred to as “working material” (e.g., by particle size in the composite working material [2, 9]). The properties of a fabricated article, in particular, strength [10], electrical conductivity [11], luminescence behavior [12], desired piezoelectric characteristics [3], etc., are specified by the composition and properties of the working material. Furthermore, it is possible to fabricate articles consisting of different functional parts such as capsules, the contents and the shell of which are printed using different working materials [13]. For example, 3D printing technique was successfully used for the manufacture of chemical reactors [14, 15], active sensing elements [16], and sorbents for the separation of gas mixtures [17]. This method can be considered as a beneficial approach to the manufacture of stationary phases for column chromatography [18].

As noted above, the formation of sophisticated structures composed of different functional parts (e.g., non-transparent casing, transparent windows, porous permeable membrane, and so on) requires different working materials. Apart from possessing the desired functional characteristics, the materials should meet a number of requirements: have a relatively high fluidity to provide the mere possibility of printing, preserve the shape up to the curing stage (performed by cooling, evaporation of the solvent, a chemical reaction, or a external physical impact, for example, irradiation), possess desirable uniformity and stability to layer separation, and undergo curing with predictable deformation (shrinkage) and retention of uniformity (without cracking).

The goal of this study is to develop compositions containing porous coordination polymers (PCPs), curable with predictable deformation, and suitable for the subsequent use for the fabrication of arbitrarily shaped 3D objects such as promising stationary phases for liquid chromatography. The need for the development of these compositions is caused by the demand for materials for microporous components of sophisticated devices and instruments fully manufactured by 3D printing. As an example, consider the manufacture of a filter. Whereas the choice of materials for manufacturing the casing is quite wide (various types of plastics, metals), the range of materials suitable for the formation of porous membranes is rather limited.

Currently, several approaches have been proposed to the fabrication of PCP-containing materials by means of 3D printing. The PCP particles can be formed on a preprinted network of an organic polymer [19] or on nanofibers, representing the major component of 3D printing ink [20]. Also, pre-synthesized PCP particles can be included into a composition used for 3D printing [21–24]. In this study, we implemented the latter approach, that is, use of PCP particles prepared in advance as components of a curable composition. This study continues the work reported in our previous publication [25].

EXPERIMENTAL

The following chemicals were used in the experiments: dimethylformamide (DMF), *l*-lactic acid, 1,4-benzenedicarboxylic acid, $K_4[Fe(CN)_6]$, zinc nitrate, zinc sulfate, tetraethoxysilane, methyl orange, rhodamine 6G, fuchsin, methanol, and 2-butanol (reagent grade) and distilled water. Starch and carboxymethylcellulose were 95% pure and β-cyclodextrin was 99% pure (other oligosaccharides and polysaccharides were present as impurities); instant gelatin with a protein content of 87.2% was used. The PCPs $[Zn_2(Bdc)(l\text{-}Lac)(DMF) \cdot DMF]_n$ (**I**) (Bdc^{2-} = 1,4-benzenedicarboxylate, $l\text{-}Lac^{2-}$ = *l*-lactate) and $\{K_2Zn_3[Fe(CN)_6]_2\}_n$ (**II**) were synthesized by known procedures [26, 27]. The size of crystals of **I** and **II** according to optical microscopy data was ~20–100 μm. The compositions were deposited on glass plates; for cleaning the surface, the plates were kept in nitric acid and washed with water prior to experiments.

Elemental analysis for C, H, N was performed on a Carlo Erba 1106 analyzer. The phase purity of **I** and **II** was confirmed using a Bruker D8 Advance powder diffractometer (CuK_α, $\lambda = 0.154$ nm). Some of the samples were irradiated with a 375-W PRK-2 UV lamp in the spectral range of 300–400 nm.

The experiments without additional binders were carried out for pastes consisting of **I** or **II** (1.0 g) and water or 2-butanol (10 mL). The working materials with binders were prepared by mixing a paste composed of **I** or **II** (1.0 g) in water (5 mL) with an aqueous solution (5 mL) of carboxymethylcellulose ($c = 0.1\%$), or tetraethoxysilane ($c = 1\%$), or starch ($c = 1\%$) (5 mL). The working material with β-cyclodextrin was prepared by mixing **I** or **II** (0.75 g), β-cyclodextrin (0.25 g), and water (5 mL) and subsequent mixing with an aqueous solution of starch (5 mL) ($c = 1\%$). In the case of gelatin-containing working material, compound **II** (1.0 g) was mixed with water (5 mL), and the resulting suspension was mixed with a 1% aqueous solution of gelatin (5 mL). After deposition of the working materials on glass, the samples were dried in air. In some experiments, glass coated with compositions containing **II**, a binder (starch, gelatin, or β-cyclodextrin), and water was UV irradiated for 6 h (the distance to the UV lamp was 1 m). For chromatography of dyes (fuchsin, methyl orange, and rhodamine 6G), methanol was used as the eluent.

RESULTS AND DISCUSSION

Working materials were obtained from microporous coordination polymers **I**, the crystal lattice of which contains pores ~5 Å in diameter [26], and **II** with a pore size of ~4 × 5 Å [27]. It is noteworthy that the choice of PCPs is not of fundamental importance for this study; it is likely that the use of other porous compounds as working material components (silica gels, aluminosilicates, carbons, etc.) would give similar results.

The working materials were deposited on glass using a syringe with a nozzle diameter of 2.5 mm, which modeled the 3D printer extruder. The consumption of the working material upon single-layer deposition was 0.2 mL/mm and the layer thickness was 2 mm before drying and 1 to 2 mm after drying. Curing of the working material was attained by evaporation of the liquid phase (similarly to the reported graphene-based compositions for 3D printing [9], copper(II) benzenetricarboxylate HKUST-1 [23]). The sample can be additionally cured by UV irradiation. An advantage of curing by liquid phase evaporatrion in the dark is the possibility of using a broad range of PCPs, in particular, compounds that are destroyed under UV irradiation. Meanwhile, UV irradiation of the working material enhances its strength and resistance against liquids, owing to irreversible photoinduced intermolecular cross-linking of the polymeric binder components (for example, polysaccharides or gelatin).

Water and 2-butanol (in the case of materials exposed to UV radiation, only water) were used as the components providing the fluidity of the working material. It was found that **I**–water and **I**–butanol (or **II**–water and **II**–butanol) suspensions (pastes) cracked upon drying (Figs. 1a, 1b), unlike the previously described HKUST-1 gel, which does not contain a binder and is cured with retention of the shape upon evaporation of the liquid component [23]. For increasing the stability of materials, addition of tetraethoxysilane, carboxymethylcellulose, gelatin, and starch to the pastes was investigated (see Experimental). The choice of these substances was based on assumption that PCP particles can be held together by the products of hydrolysis of tetraethoxysilane (hydrated SiO_2), polysaccharide molecules (starch or carboxymethylcellulose), or gelatin protein molecules, in particular, collagen.

The use of carboxymethylcellulose and tetraethoxysilane did not lead to the expected result: the layer still cracked upon drying (Figs. 1c, 1d). In the case of starch and gelatin, visually homogeneous samples were obtained (Fig. 1e). Cracking of the material during drying is caused by its substantial compaction upon removal of the solvent. The function of starch and gelatin is, probably, to stick the PCP particles together; hence, after evaporation of water, the particles retain positions in which they were located in the

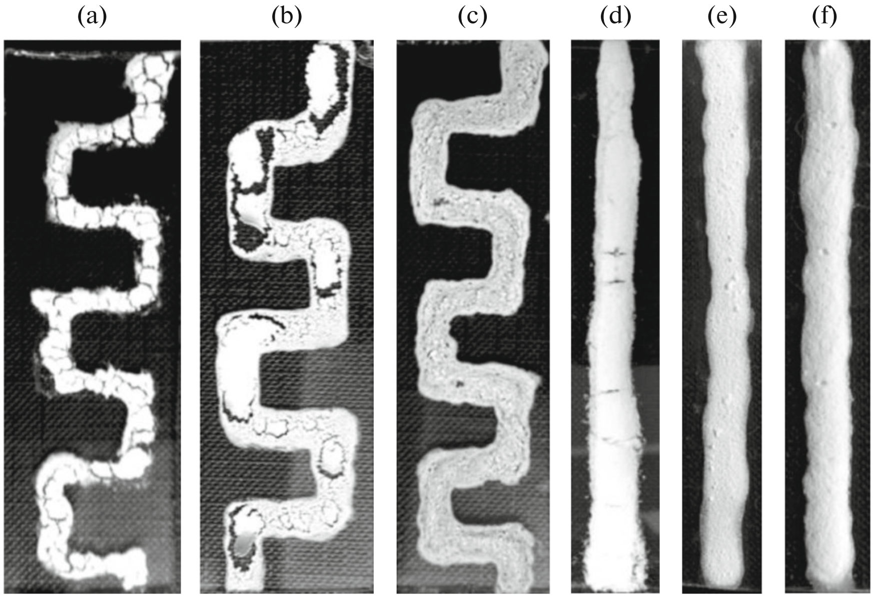

Fig. 1. Layers produced by a single deposition on glass of compositions consisting of **I** and (a) water, (b) 2-butanol, (c) carboxymethylcellulose plus water, (d) tetraethoxysilane plus water, (e) starch plus water, and (f) β-cyclodextrin, starch, and water.

hydrated composition. Unlike the present study, in a previous study, the use of methylcellulose as a component of 3D printing ink in a composition containing PCPs also resulted in the fabrication articles that were cured without deformation [22]. Presumably, retention of PCP particles in definite positions during curing is, to so some extent, due to the formation of hydrogen bonds between the polymeric starch molecules [28] or protein molecules present in gelatin adsorbed on PCP microparticles. However, the layer formed using starch proved to be unstable to methanol: attempted chromatography of the dye (fuchsin) resulted in the loss of mechanical strength and crumbling of the sample. A sample resistant to methanol was fabricated using a four-component working material consisting of PCP (**I** or **II**), β-cyclodextrin, starch, and water (Fig. 1f) with the cyclodextrin to starch weight ratio being 5 : 1, or using the paste of **II** and an aqueous solution of gelatin. The samples formed in this way are not destroyed and preserve the shape upon elution with methanol of some amine dyes: fuchsin, rhodamine G, or methyl orange (Fig. 2). The successive deposition of working material layers based on PCP (**I** or **II**), β-cyclodextrin, and starch allows increasing the thickness of the porous material (Fig. 3) with the formation of arbitrarily shaped articles, e.g., a part of a tube (Fig. 4). The possibility of chromatographic separation of dyes on the obtained compositions containing PCP particles and a binder is consistent with the results of a previous study [24], which demonstrates that even in a composition containing the 2-phenoxyethyl acrylate and polyethylene glycol diacrylate copolymer, HKUST-1 particles remain available for adsorbates.

Despite the possibility of dye chromatography on the obtained samples with methanol as the eluent, the samples are gradually destroyed at the sites of direct contact with liquid methanol. In order to increase the stability of the cured compositions to the eluent, we studied UV irradiartion of compositions containing **II**. Compound **II** was chosen because of the expected higher stability of inorganic PCPs to UV radiation compared with compound **I**, containing organic ligands. It was found that irradiation of starch- and gelatin-containing compositions cured upon solvent evaporation enhances their stability to the eluent, which is manifested as the absence of visible deformations with retained ability to act as the stationary phase for chromatography (Figs. 2b, 2c). Unlike compositions that are cured only via water evaporation, the samples subjected to UV radiation, including articles of sophisticated shape, showed no visual signs of destruction upon dye elution with methanol (for example, the tubes shown in Fig. 4). Meanwhile, irradiation of β-cyclodextrin-containing compositions led to complete destruction of the sample, which was manifested as cracking, disruption of integrity, and separation from the glass substrate. The addition of gelatin to the β-cyclodextrin-containing compositions did not prevent the sample destruction after UV irradiation.

Thus, we demonstrated the conceptual possibility of fabrication of compositions containing microporous coordination polymers and curable with a pre-

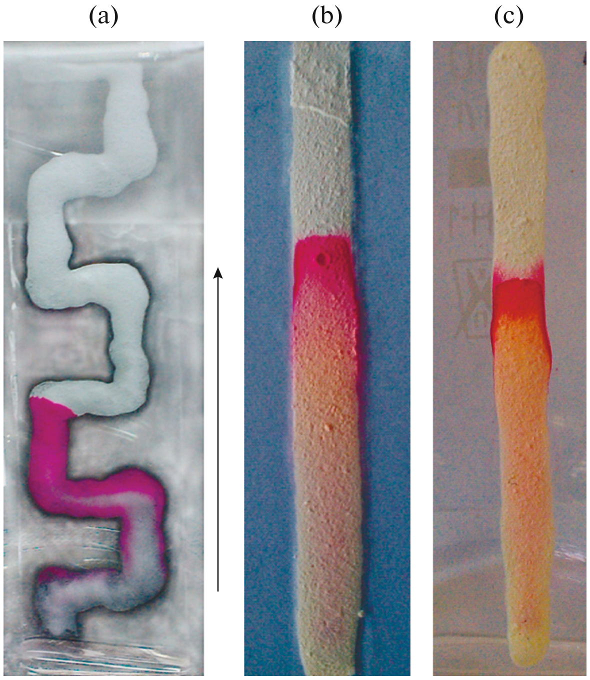

Fig. 2. Results of chromatography: fuchsin on the sample obtained upon curing of the working material composed of (a) **I**, β-cyclodextrin, starch, and water; (b, c) rhodamine 6G on the sample obtained on curing and UV irradiation of the working material based on **II** and containing (b) starch and (c) gelatin. The arrow shows the direction of eluent movement; in the experiment, the plate was arranged vertically.

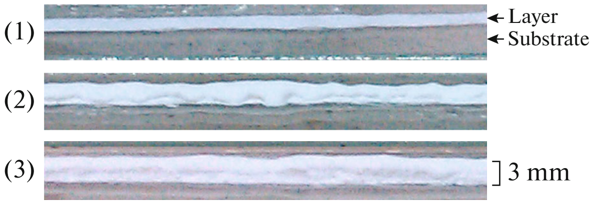

Fig. 3. Increase in the sample thickness upon deposition of several layers of the working material consisting of **II**, β-cyclodextrin, starch, and water (the numerals in parentheses corresponds to the number of layers).

dictable deformation, which can be considered as the prototypes of porous objects suitable for fabrication by 3D printing. It was found that the working material containing PCPs and polysaccharides (β-cyclodextrin and starch) or gelatin are not virtually distorted upon curing and subsequent action of methanol. UV irradiation of starch- or gelatin-containing compositions makes them more stable to swelling in methanol.

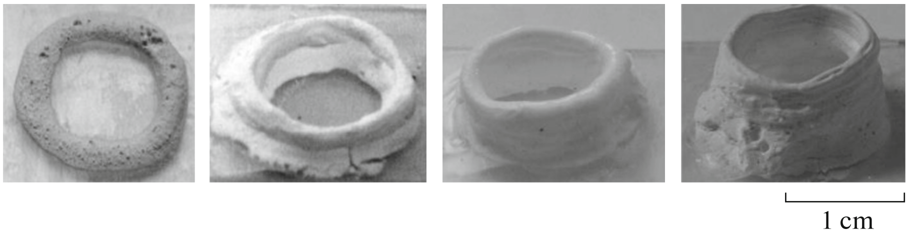

Fig. 4. Increase in the sample thickness upon deposition of several layers of the working material consisting of **II** and gelatin followed by UV irradiation.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Hong, S., Sycks, D., Chan, H.F., et al., *Adv. Mater.*, 2015, vol. 27, p. 4035.
2. Rutz, A.L., Hyland, K.E., Jakus, A.E., et al., *Adv. Mater.*, 2015, vol. 27, p. 1607.
3. Kim, K., Zhu, W., Qu, X., et al., ACS *Nano*, 2014, vol. 8, no. 2014, p. 9799.
4. Jungst, T., Smolan, W., Schacht, K., et al., *Chem. Rev.*, 2016, vol. 116, no. 3, p. 1496.
5. Lin, D., Nian, Q., Deng, B., et al., *ACS Nano*, 2014, vol. 8, no. 2014, p. 9710.
6. Gross, B.C., Erkal, J.L., Lockwood, S.Y., et al., *Anal. Chem.*, 2014, vol. 86, p. 3240.
7. 3D printing. http://www.oxforddictionaries.com/definition/american_english/3D-printing.
8. Parkinson, H.J., 3Doodler 2.0 printing pen makes drawing in air a reality, *The Guardian*., January 6, 2015.
9. Kim, J., Chang, W.S., Kim, D., et al, *Adv. Mater.*, 2015, vol. 27, p. 157.
10. Compton, B.G. and Lewis, J.A., *Adv. Mater.*, 2014, vol. 26, p. 5930.
11. Muth, J.T., Vogt, D.M., Truby, R.L., et al., *Adv. Mater.*, 2014, vol. 26, p. 6307.
12. Kong, Y.L., Tamargo, I.A., Kim, H., et al., *Nano Lett.*, 2014, vol. 14, p. 7017.
13. Gupta, M.K., Meng, F., Johnson, B.N., et al., *Nano Lett.*, 2015, vol. 15, p. 5321.
14. Kitson, P.J., Marshall, R.J., Long, D., et al., *Angew. Chem., Int. Ed. Engl.*, 2014, vol. 53, p. 12723.
15. Symes, M.D., Kitson, P.J., Yan, J., et al., *Nature Chem.*, 2012, vol. 4, p. 349.
16. Wu, T., Gray, E., and Chen, B., *J. Mater. Chem. C*, 2018, vol. 6, p. 6200.
17. Thakkar, H., Lawson, S., Rownaghi, A., et al., *Chem. Eng. J.*, 2018, vol. 348, p. 109.
18. Kalsoom, U., Nesterenko, P.N., and Paull, B., *Trends Anal. Chem.*, 2018, vol. 105, p. 492.
19. Wang, Z., Wang, J., Li, M., et al., *Sci. Rep.*, 2014, vol. 4, no. 5939.
20. Sultan, S., Abdelhamid, H.N., Zou, X., and Mathew, A.P., *Adv. Funct. Mater.*, 2018, vol. 29, P. 1805372.
21. Young, A., Guillet-Nicolas, R., Marshall, E., et al., *Chem. Commun.*, 2019, vol. 55, p. 2190.
22. Lefevere, J., Claessens, B., Mullens, S., et al., *ACS Appl. Nano Mater.*, 2019, vol. 2, p. 4991.
23. Lim, G., Wu, Y., Shah, B., et al., *ACS Mater. Lett.*, 2019, vol. 1, p. 147.
24. Haveli, O., Tan, J.M.R., Lee, P.S., and Magdassi, S., *Adv. Sustainable Syst.*, 2018, vol. 2, p. 1700150.
25. Sotnik, S.A., Kolotilov, S.V., Satskaya, Yu.A., et al., Ukr. Patent no. 107235, 2016.
26. Dybtsev, D.N., Nuzhdin, A.L., Chun, H., et al., *Angew. Chem. Int. Ed.*, 2006, vol. 45, p. 916.
27. Cartraud, P., Cointot, A., and Renaud, A., *J. Chem. Soc., Faraday Trans.*, 1981, vol. 77, p. 1561.
28. *Starch-Based Polymeric Materials and Nanocomposites: Chemistry, Processing, and Applications*, Ahmed, J., Tiwari, B.K., Imam, S.H., Rao, M.A., Eds., Boca Raton: CRC, 2012.

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