Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

3D Printing of Polymeric Materials Based on Photo-RAFT Polymerization

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Materials

Poly (ethylene glycol) diacrylate (PEGDA 250) (average M_n 250 g/mol), tetra (ethylene glycol) diacrylate (TEGDA), and *n*-butyl acrylate (BA) were purchased from Sigma Aldrich and deinhibited by passing through a column of basic alumina. dibenzyl trithiocarbonate (DBTTC), 4-cyano-4-[(dodecylsulfanylthiocarbonyl) sulfanyl] pentanoic acid (CDTPA), phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (TPO), 2,2′-azobis(2-methylpropionitrile) (AIBN) and 1-pyrenemethyl methacrylate (PyMA) were purchased from Sigma Aldrich and used as received. All the other reagents were used as received unless otherwise specified.

Characterization

Scanning Electron Microscopy (SEM) was performed using a FEI Quanta 200 field emission environmental SEM. A scanning voltage of 10 KeV and a spot size of 3 was used. Samples were characterized with a working distance of 11 – 13.5 mm. A low vacuum secondary electron detector was used.

Photo Differential Scanning Calorimetry (photo-DSC) was performed using a commercial Netzsch Photo-DSC consists of a DSC3500 Sirius unit coupled with Klerex Delolux 04 light source (315-500 nm). Samples were placed into an aluminium pan and the exposure time was set between 30 seconds and 16 min, depending on the nature of resin formulation. Samples were measured under isothermal conditions at 25˚C and a nitrogen purge flow of 250 ml/min. The light intensity was set to 9.9 W cm^{-2}.

The contact angle (CA) measurement was performed using a Contact Angle Meter (CAM) 100 by dispensing a water droplet with a threaded micro syringe. The optical images of the water contact angle were recorded and analysed by using the CAM 100 software. The program uses a Young-Laplace equation to calculate the drop shape. The values of the parameters were repeated until an acceptable compromise between the actual drop profile and the model was achieved. The measurements were performed at ambient room temperature and pressure.

A modified ANYCUBIC Photon (https://www.anycubic.com/) DLP 3D printer was used for 3D fabrication of RAFT-based resin formulations, where LED lights (λ_{max} = 405 nm, 1.8 mW/cm^2) were focused on the bottom surface of the resin vat. Photo-curing occurs between

the bottom of the vat and the motorized build platform through an in-house built mask. 3D printing parameters such as layer exposure times (8 - 60 min) and layer thickness (20-100 μm) were set using ANYCUBIC Photon Slicer software. The 3D models were designed using an online software provided by Autodesk® Tinkercad™, which were then transferred to the slicing software.

Experimental Section

1.1 Preparation of a Conventional Photo-Curable Resin

A solution containing PEGDA (36.63g, 146.52 mmol) and TPO (~ 2 wt%) was prepared for photo-DSC measurements.

1.2 General Procedure for 3D Printing of Visible Light-Curable RAFT-Based Resin Formulations;

Entry 1 to entry 3:

A molar ratio of [PEGDA]/[CDTPA] = 100:1 was prepared by dissolving CDTPA (627.30 mg, 1.55 mmol) into PEGDA (38.85 g, 155.40 mmol) and subsequently introduced into the 3D printer vat. Depending on the pre-defined parameters different 3D printed objects were obtained (**Table 1**).

Entry-4 to entry-7:

A molar ratio of [PEGDA]/[CDTPA] = [50]:[1] was prepared by dissolving CDTPA (716.92 mg, 1.78 mmol) into PEGDA (22.20 g, 88.80 mmol) and subsequently introduced into the 3D printer vat. Depending on the pre-defined parameters different 3D printed objects were obtained (**Table 1**).

Entry 8 to entry-11:

A molar ratio of [PEGDA]/[DBTTC] = 50:1 was prepared by dissolving DBTTC (1.04 g, 3.58 mmol) into PEGDA (44.80 g, 179.20 mmol) and subsequently introduced into the 3D printer

vat. Depending on the pre-defined parameters different 3D printed objects were obtained (**Table 1**).

Entry-12:

A molar ratio of [TEGDA]/[BA]/[DBTTC] = 45:5:1 was prepared by dissolving DBTTC (710.99 mg, 2.45 mmol) into TEGDA (33.30 g, 110.15 mmol) and BA (1.57 g, 12.24 mmol), and subsequently introduced into the 3D printer vat for 3D printing of entry 12.

Note 1: All these formulations were sonicated until the RAFT agents were all dissolved in the monomer.
Note 2: All the formulations were degassed prior to the printing process, while the 3D printing processes were performed under a nitrogen environment inside a glovebox.

1.3 General Procedure for the Post-Printing Transformation of 3D Printed Objects; e.g. PyMA Monomer Insertion into the 3D Printed "RAFT" Word:

A growth medium containing PyMA (84.2 mg, 0.28 mmol), AIBN (23.16 mg, 0.14 mmol), and DMSO (56.41 μL, 5 M concentration) was prepared. The "RAFT" word (which was initially printed using the parameters and conditions of entry 9) was soaked in this solution for 24 h and then degassed for 20 min at room temperature, before being heated at 70˚C for 24 h in an oil bath. After the reaction, the pyrene modified "RAFT" word was extensively washed in DMSO to remove unreacted PyMA monomers.

e.g. BA Monomer Insertion into a Disc-Shape 3D Printed Object:

A growth medium containing BA (164.17 mg, 1.28 mmol), and DMSO (128 μL, 10 M concentration) was prepared. The parent 3D printed disk was then soaked in this solution for 24 hours and degassed for 20 minutes at room temperature, before being irradiated under a blue LED light (λ_{max} = 460 nm, 0.7 mW/cm^2) for 6 hrs. After the photo-growth reaction, the modified object was removed and was extensively washed in DMSO to remove unreacted BA monomers.