**Supporting information**

# Dissipative particle dynamics simulation study on ATRP-brush modification of variably shaped surfaces and biopolymer adsorption

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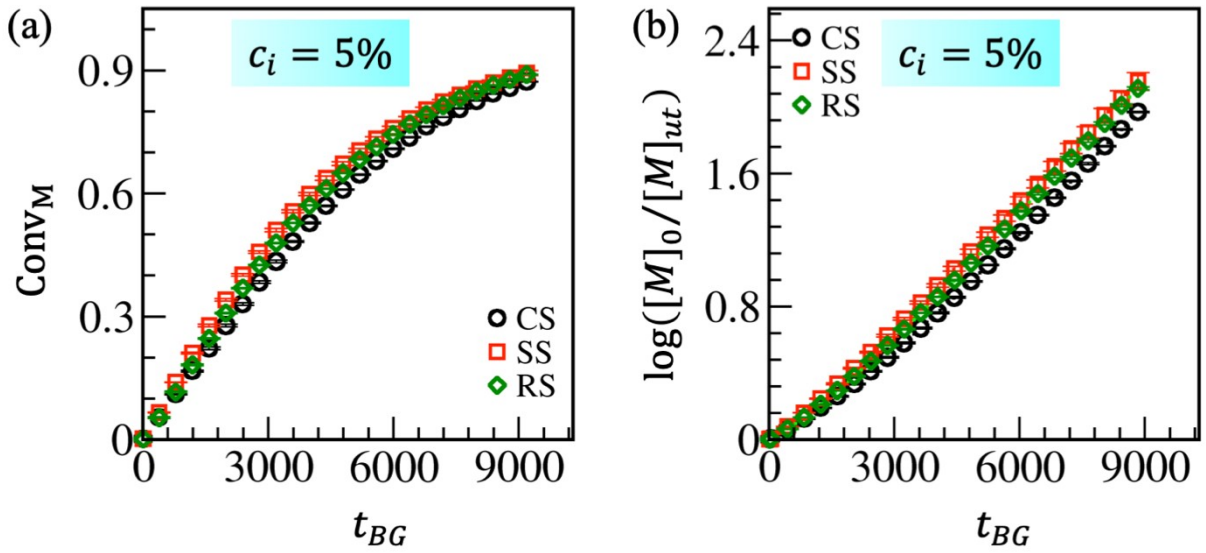


**Figure S1**: Comparison of temporal variation of $Conv_M$ in (a), and $log\left([M]_0/[M]_{ut}\right)$ in (b) at the cup surface (CS) in black, spherical surface (SS) in red, and rectangular surface (RS) in green curves for $c_i = 5.0\%$ embedded on their surfaces. (a) The monomer conversion shows a linear behavior at early times (as shown in Fig. 2 and Fig. 5) and converges towards one at late times. (b) Shows the nearly linear dependence of $log\left([M]_0/[M]_{ut}\right)$ versus time.

## 1. Experimental procedure

### 1.1. Materials

Polylactide (3052D, $M_n$ - 116,000 g/mol) is obtained from Nature Work. Methyl Methacrylate (>99.0%), 2-hydroxy ethyl methacrylate (>95.0%), 2-dimethyl aminoethyl methacrylate (>98.5%) are procured from TCI. The acrylate monomers are passed through a column of basic alumina to remove the inhibitor. Copper (I) bromide is supplied from Spectrochem, and bromopropionyl bromide are procured by TCI. Copper bromide (I) is washed with glacial acetic acid and ethanol, respectively, for purification. Fischer Scientific supplies

basic alumina neutral alumina, dimethylformamide, and ethylene diamine tetraacetate. Chloroform and Tween-20 are procured from Merck. Methyl bromo propionate and Pentadiethylene tetraacetate (PMDETA) are obtained from Sigma Aldrich. α-Glucosidase (Maltase) extracted from yeast (which contained 100U (active)/mg), p-nitrophenyl-α-D-glucopyranoside (α-PNPG, extra pure, 98%), and Sisco Research Laboratories supply glutathione. Rhodamine B dye is purchased from India Mart.

### 1.2. Fabrication of spherical, cup-shaped, and disc-shaped particles and their surface modification by growing Poly(DMAEMA) Brushes

First, copolymerization of methyl methacrylate and 2-hydroxy ethyl methacrylate (HEMA) is carried out by the bulk ATRP method. The hydroxyl groups (in HEMA unit) are converted to ATRP-initiating moiety (BEMA unit) by reacting them with bromopropionyl bromide to yield poly($MMA_{0.9}$-co-$BEMA_{0.1}$) ($M_n$: 9155 g/mol; PDI:1.38) as discussed in our previous publication.[1] Then, spherical, cup-shaped, and disc-shaped particles are made via the electrohydrodynamic jetting (EHDJ) technique. A polymer solution is obtained by a blend of 75 wt % PLA and 25 wt % poly(MMA-co-BEMA) dissolved in a solvent system (chloroform: DMF - 97:3). This is sprayed at different concentrations, flow rates, and applied voltage (details of solution/processing parameters are given in Table S1). Then, poly(DMAEMA) chains (polymer brushes) are grown from the surface of spherical, cup-shaped, and disc-shaped particles using the "grafting from" surface-initiated atom transfer radical polymerization (SIATRP) as discussed in our previous paper.[1] Except spherical, cup and disc-shaped particle formation and brush modifications have already been discussed in our earlier publications.[1,2]

| **Shape** | **Concentration of polymer solution (w/v%) ((75%PLA +25%poly(MMA-co-BEMA))** | **Flow rate (ml/h)** | **Voltage (kV)** |
|---|---|---|---|
| Spheres | 4.5 | 0.5 | 8.5 |
| Cups | 1 | 1 | 9 |
| Discs | 3 | 1.5 | 9 |

Table S1: Solution/Processing parameters to fabricate spheres, cups, and discs.

### 1.3. Immobilization of the α-Glucosidase Enzyme onto the brush modified spherical, cup-shaped, and disc-shaped particles[2]

First, α-glucosidase is mixed in a solvent (phosphate buffer solution (pH ~ 6.8)) at a concentration of 0.8 mg/mL or 80 U/mL (one unit (U) enzyme may be defined as the amount which can catalyze the conversion of 1 μmol of α-PNPG in a minute)[2]. Initially, particles (1mg) are dispersed in 100 μL (0.08mg/mL) in a 1.5 mL centrifuge tube, and particles are stirred on

a plate shaker for 1 h at room temperature. After 1h, particles are collected in a centrifuge at 10,000 rpm and washed three times. The immobilized enzyme amount (active units) is obtained by deducting the amount of the enzyme present in the supernatants (initial supernatants and supernatant obtained on washing the particles) from the initial solution. Then, α-PNPG (substrate) is taken for enzyme activity determination, which gets hydrolyzed by the α-glucosidase enzyme to release p-nitrophenol (p-NP).[2] Thus, the amount (mmoles) of released *p*-NP is identified by UV/vis spectroscopy at 400 nm (a calibration curve is already prepared using pure *p*-nitrophenol)[2]. The experiments are performed in triplicate.

### 1.4. Characterization Methods.

UV absorbance is done on Synergy h1, microplate reader. CLSM images are taken on a confocal laser scanning microscope (CLSM), Leica LAS 2.6.0 build7266. Bright-field images are taken on an optical microscope (Model -Olympus IX73). The samples for both pictures are prepared by mounting dispersed particles on a glass slide and then covering the drop with coverslips.

## 2. References:


1 Ifra and S. Saha, Fabrication of topologically anisotropic microparticles and their surface modification with pH responsive polymer brush, *Materials Science and Engineering*, 2019, **104**, 109894.

2 Ifra, A. Singh and S. Saha, High Adsorption of α-Glucosidase on Polymer Brush-Modified Anisotropic Particles Acquired by Electrospraying - A Combined Experimental and Simulation Study, *ACS Applied Bio Materials*, 2021, **4**, 7431–7444.