Supplementary Information

Open-aired Synthesis of Star-shaped Poly[2-(Methacryloyloxy)Ethyl Trimethylammonium Chloride)]

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Experimental section

Materials and methods

[2-(methacryloyloxy)ethyl]trimethylammonium chloride solution (META, Sigma-Aldrich, 80 wt.% H_2O), 2,2'-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044, TCI, >98%) TCI), glucose (TCI, 98%), glucose oxidase (GOx) (Type XS, Sigma-Aldrich), copper (II) chloride $CuCl_2$ (Sigma-Aldrich, 99.995%) tris(2-pyridylmethyl)amine (TPMA, Sigma-Aldrich, >98%) Sigma-Aldrich, sodium pyruvate (TCI, >97% TCI), 2-hydroxyethyl 2-bromoisobutyrate (HO-EBiB, Sigma-Aldrich, 95%), ethanol (STANLAB, 99,9%), Dialysis Tubing (Spectra/Por 3, 3.5 kD MWCO).

0.01 M Phosphate buffer saline (PBS, pH 7.4, Sigma-Aldrich) was prepared according to the following procedure: one tablet was dissolved in 200 mL of deionized water yielding 0.01 M phosphate buffer saline (0.0027 M potassium chloride and 0.137 M sodium chloride).

Synthesis of star-shaped polymers (example for META, 800:1 molar ratio to initiator)

The reaction proceeded in an opened-air glass vial. First, monomer META (0.566 mL of 80% META solution in water, 2.41 mmol) was introduced to the vial. Subsequently, glucose (0.18 g, 1 mmol) and GOx (0.0016 g, 10 nmol) were added to the reaction mixture. GOx functioned as a catalyst in the oxidation of β-D-glucose to β-D-glucono-1,5-lactone and hydrogen peroxide (H_2O_2), utilizing molecular oxygen as an electron acceptor. Following this, the reaction mixture was topped up with PBS to a total volume of 5 mL, and the initiator 8-HP-β-CD (7.69 mg, 3.81 μmol) was added either as a solid (entries CP1, CP4, CP6, CP7, C10, and C11) or dissolved in 1.5 mL of methanol (entries C2, C3, C5, C8, and C9). After the components of the reaction mixture had dissolved, VA-044 (0.88 mg, 2.7 μmol) was added, and a solution of $CuCl_2$/TPMA in DMF (4.76 μL, comprising 0.177 μmol $CuCl_2$ and 0.531 μmol TPMA The reaction sequence proceeded with the incorporation of sodium pyruvate (55.02 mg, 0.5 mol), followed by the addition of 4.995 mL of PBS (3.495 mL for entries with initiator dissolved in methanol). Finally, the reaction mixture was thoroughly homogenized and placed in an oil bath at 45°C for 2 hours. Next, the reaction mixture was diluted with 25 mL of ethanol and passed through a neutral aluminum oxide (Al_2O_3) column. The obtained solution was dialyzed against deionized water, within 24 hours. The obtained dialysate was lyophilized, and the final product was a white foam (0.269 g, yield 53.79%).

Nuclear Magnetic Resonance (NMR)

^1H NMR spectra of the synthesized polymers and reaction mixtures were collected on Varian Inova 600 MHz spectrometer (Palo Alto, CA, USA) at 25 °C using D_2O. Samples were prepared by dissolving about 7 mg of the solid sample in 0.7 cm^3 of D_2O or 0.12 cm^3 of reaction mixture in 0.58 cm^3 D_2O.

Size Exclusion Chromatography (SEC)

Number-average molecular weight ($M_{n,\ SEC}$) and dispersity index (Đ) were determined by size-exclusion chromatograph (Thermo Fisher Scientific, Waltham, MA, USA) equipped with a precolumn TSKgel Guardian SuperMP (HZ)-H (4.6 mm × 2 cm, particle size of 6 μm), two columns of TSKgel SuperMilipore HZ-H (4.6 mm × 15 cm, particle size 6 μm), and a differential refractometer RefractoMax 521 detector. The analysis was conducted at 40 °C in deionized water with a flow rate of 0.45 mL/min using poly(ethylene oxide)/poly(ethylene glycol) standards ranging from 982 to 969,000 g/mol.

Differential Scanning Calorimetry (DSC)

Thermal analysis was performed on the obtained compounds using Mettler-Toledo DSC3 differential scanning calorimeter equipped with an MS105U analytical balance (Greifensee, Switzerland). The samples were placed in 40 μL aluminum standard crucibles with a lid and pin. The temperature range was from −40 °C to 250 ° with a heating rate of 10 °C per minute.

Spin-coating

The spin-coating method was used for applying polymeric thin films to 22 mm x 22 mm glass plates utilizing a Laurell WS-650MZ Spin Coater. Before spin-coating, glass plates were washed in an ultrasonic bath filled with acetone for 15 minutes, carefully transferred to an exicator, and left for 24 hours. Glass plates prepared in this manner were utilized for spin-coating in which a volume of 60 µL of polymer solution was spun at rotational speeds of either 1500 rpm or 5000 rpm. Finally, the plates were transferred into an exicator and left for 24 hours.

Contact angle measurement

The water contact angle (WCA) and interfacial tension (IFT) of the obtained polymeric coatings were measured on the Goniometer Data Physics OCA 15EC via the sessile drop method. The tests were carried out with SCA20 software. To ensure replicability, the methodology involved the deposition of three distinct droplets, each comprising 6 µL, onto every plate. The data represent the mean values derived from these three drops.

Atomic Force Microscopy (AFM)

The analysis of topography was conducted using a BioScope Catalyst atomic force microscope from Veeco/Digital Instruments, which was equipped with a NanoScope V controller. The preparation of samples involved the following steps. The BioScope Catalyst from Bruker was used to perform measurements in contact mode. A ScanAsyst-Air cantilever with a spring constant of 0.4 N m^{-1} was utilized for these measurements. The scanning speed was 0.65 µm/s, and the scan resolution was 512x512. All images were captured under ambient conditions. The data analysis was performed using NanoScope version 1.80 and ImageJ Fiji software. Surface roughness was characterized by arithmetic mean deviation of the profile from the mean line (R_a), root mean square of a surface (R_q), and coating thickness (D). Coating thickness values were determined by scratch-and-scan method, which involves measuring the height of the furrow originated from scratching the polymeric film[32]. The R_a and R_q values were calculated according to the equations:

$$R_a = \frac{1}{N} \sum_{j=1}^{N} |Z_j|, \qquad R_q = \sqrt{\frac{\sum Z_j^{\,2}}{N}}$$

Where: Z_j - height at each pixel position along the profile line, N - maximum number of pixels along each scan of the profile line, in our case this number was 512.

Supplementary Figures and Tables section

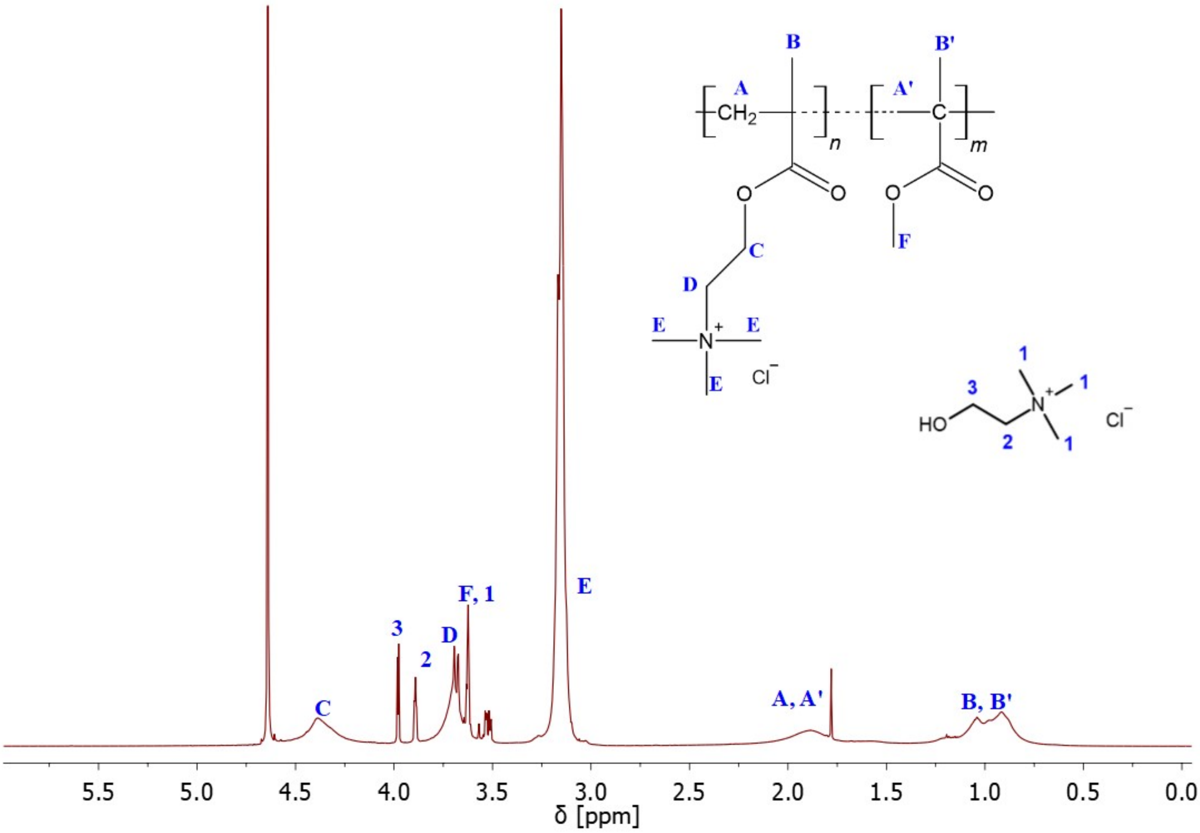

Figure S1. ^{1}H NMR (600 MHz, D_2O) spectra of exemplary 8-arm star polymer C8.

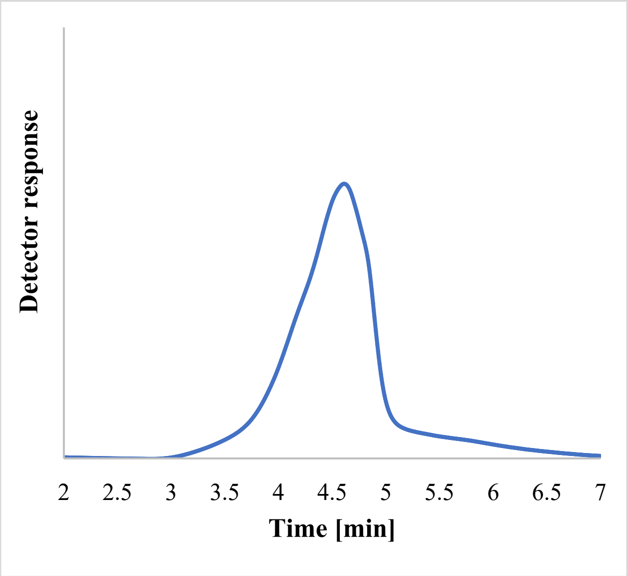

Figure S2. SEC traces of linear PMETA from RID detector.

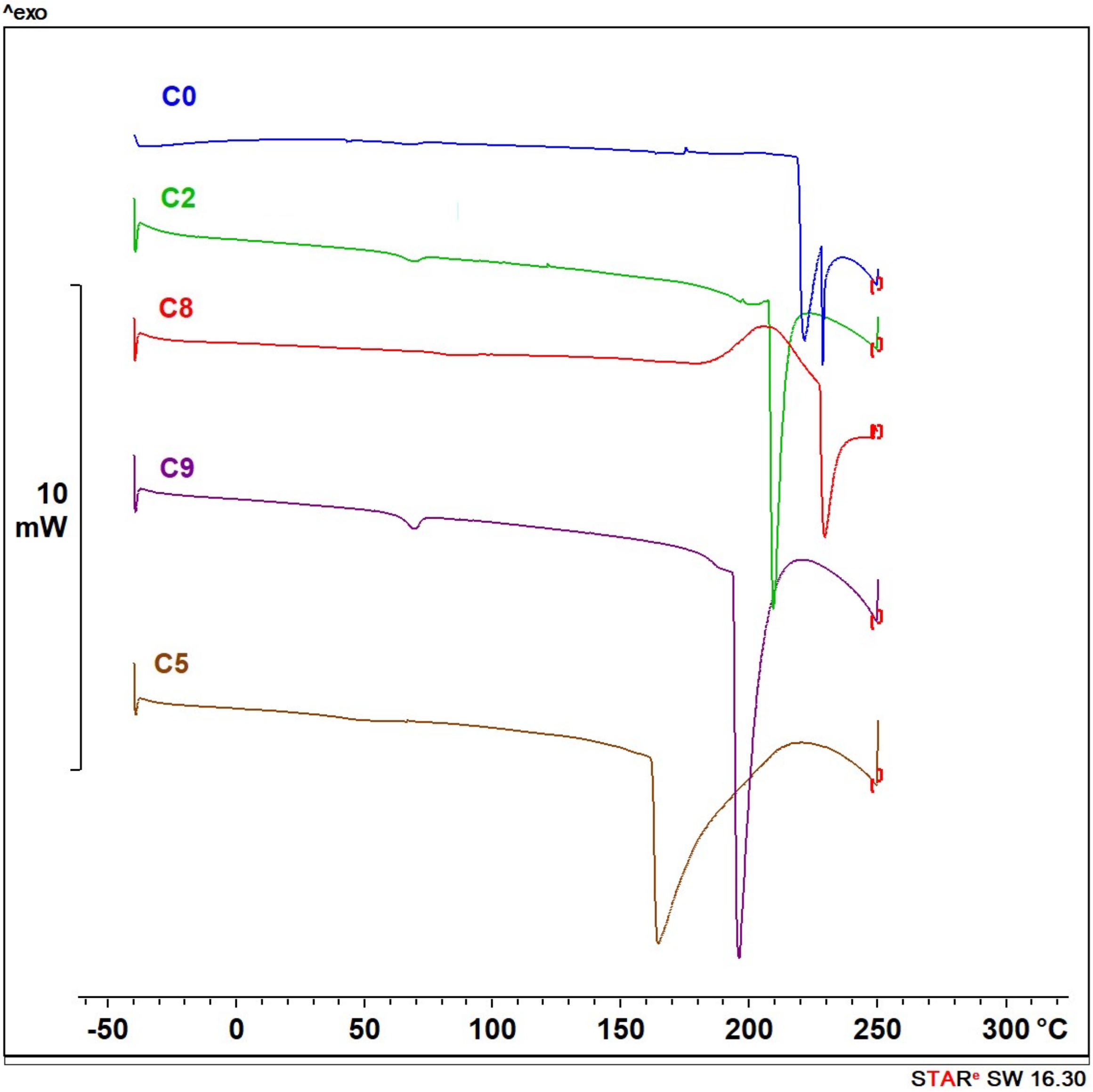

Figure S3. DSC thermograms for linear (C0) and star-shaped (C2, C5, C8, and C9) PMETAs'.

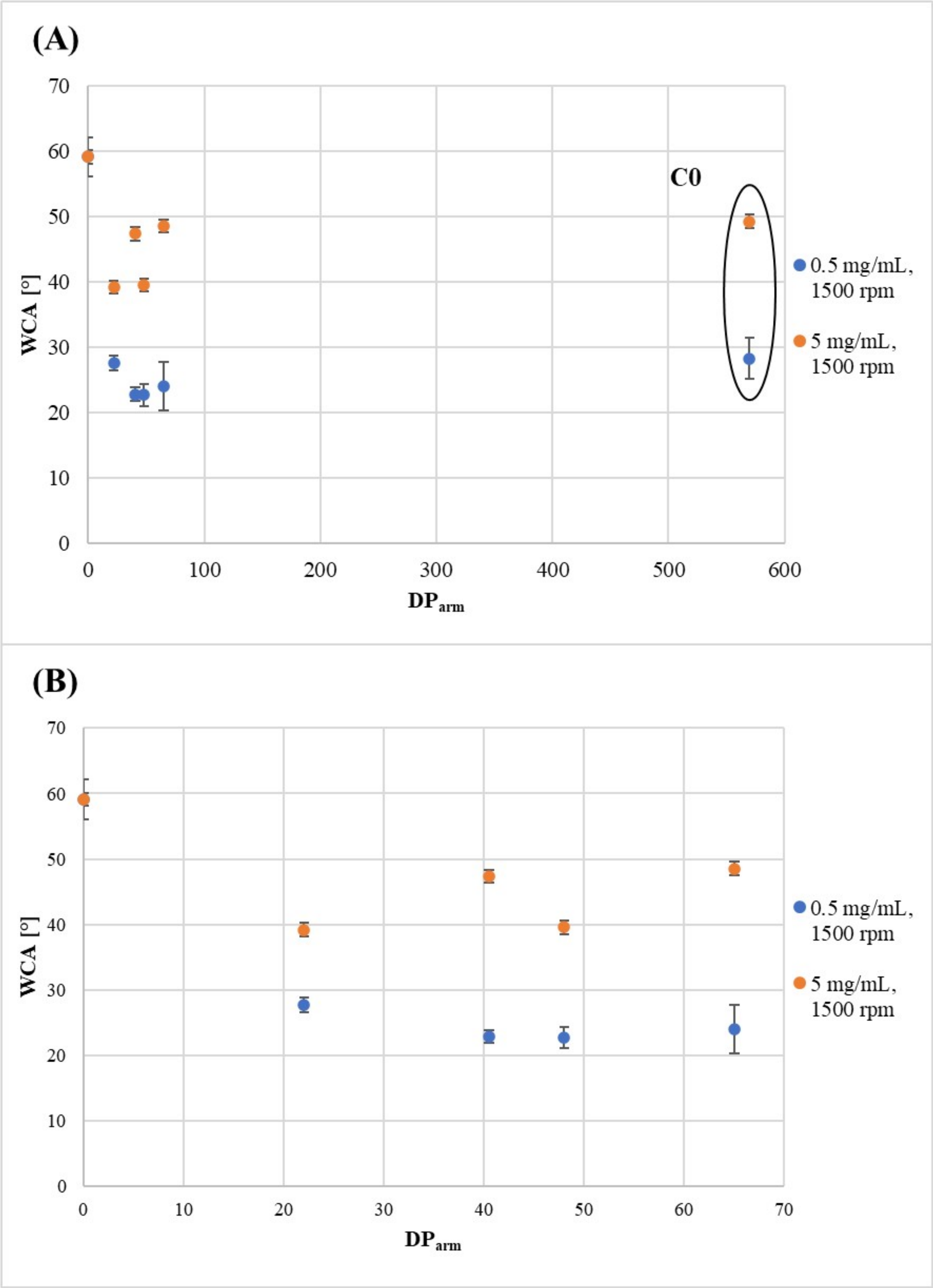

Figure S4. WCA as a function of DP per arm of obtained polymers at a concentration of 0.5 mg/mL and 5 mg/mL (A), a subset of the top graph showing only star-shaped polymers (B).

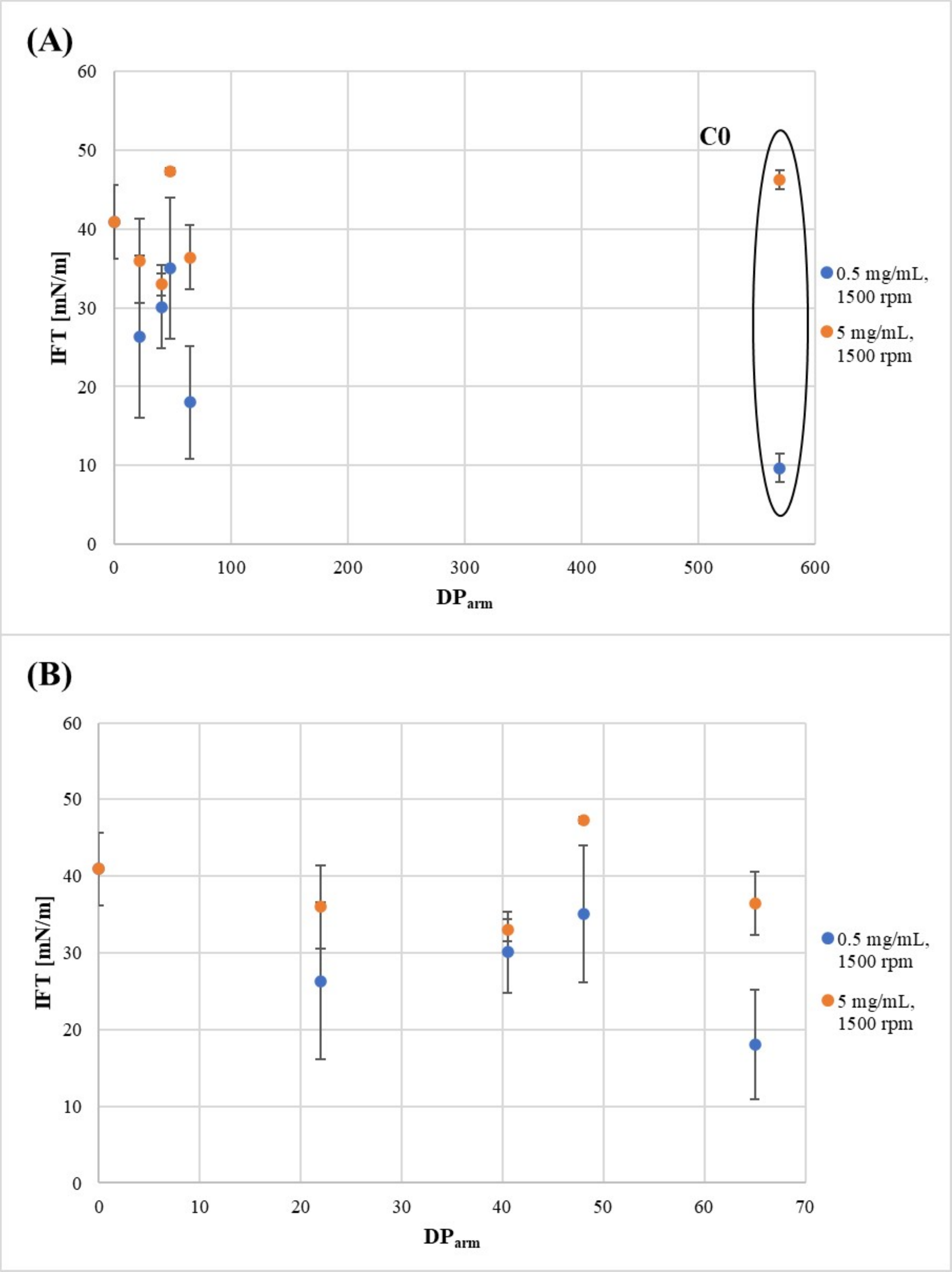

Figure S5. IFT as a function of DP per arm of obtained polymers at a concentration of 0.5 mg/mL and 5 mg/mL (A), a subset of the top graph showing only star-shaped polymers (B).

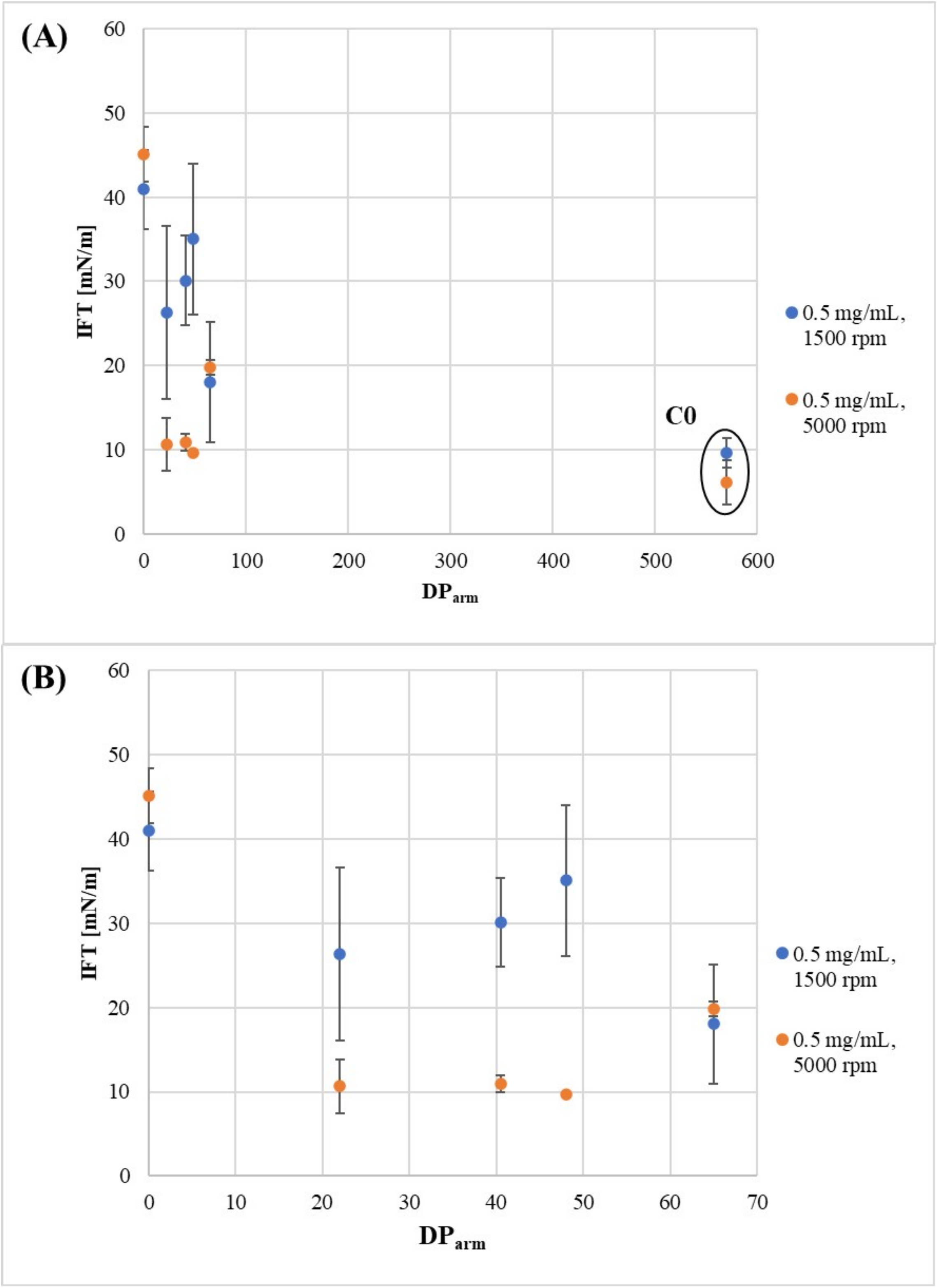

Figure S6. IFT as a function of DP per arm of obtained polymers at a concentration of 0.5 mg/mL (A), a subset of the top graph showing only star-shaped polymers (B).

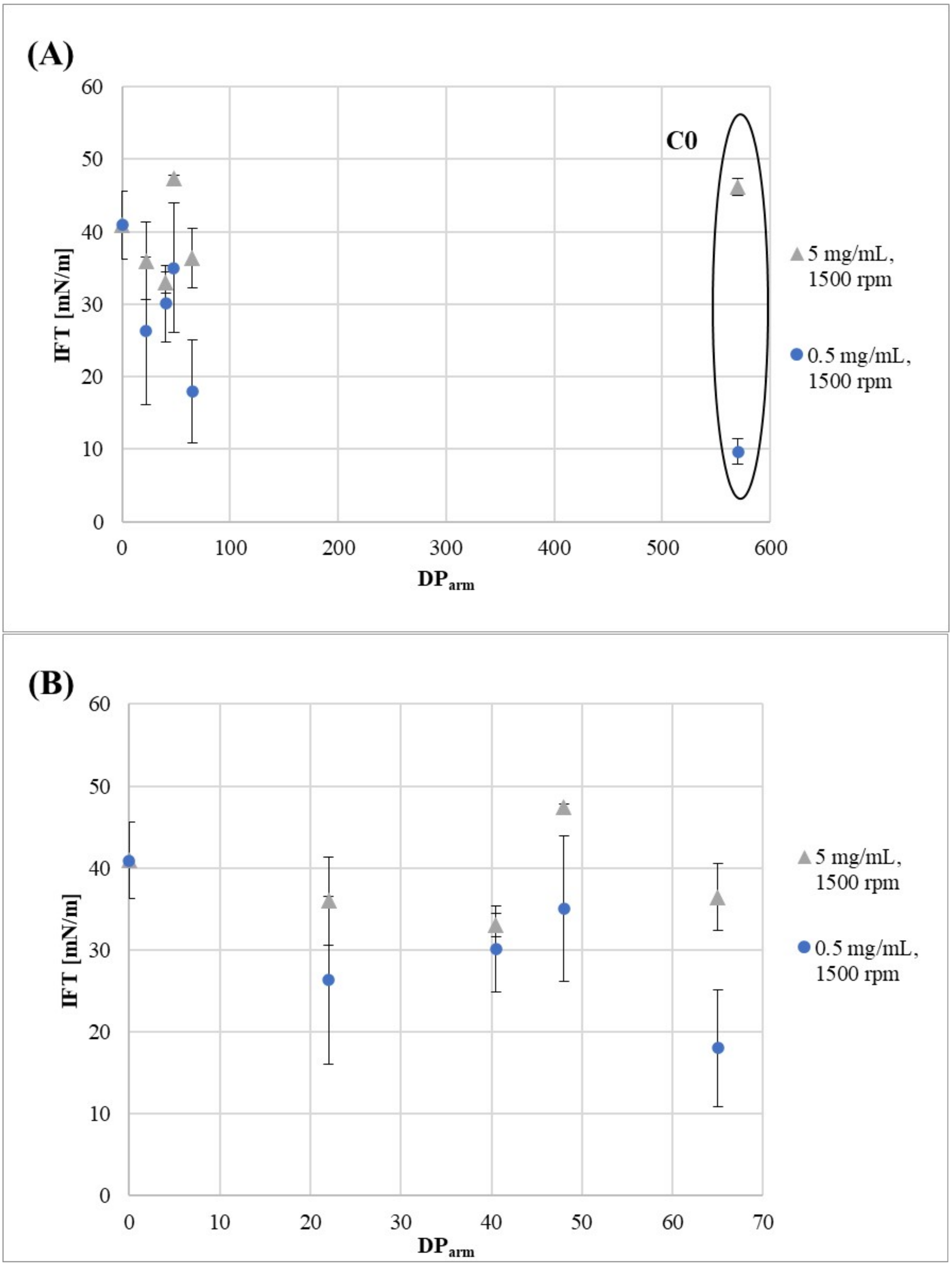

Figure S7. IFT as a function of DP per arm of obtained polymers at a concentration of 0.5 mg/mL and 5 mg/mL (A), a subset of the top graph showing only star-shaped polymers (B).

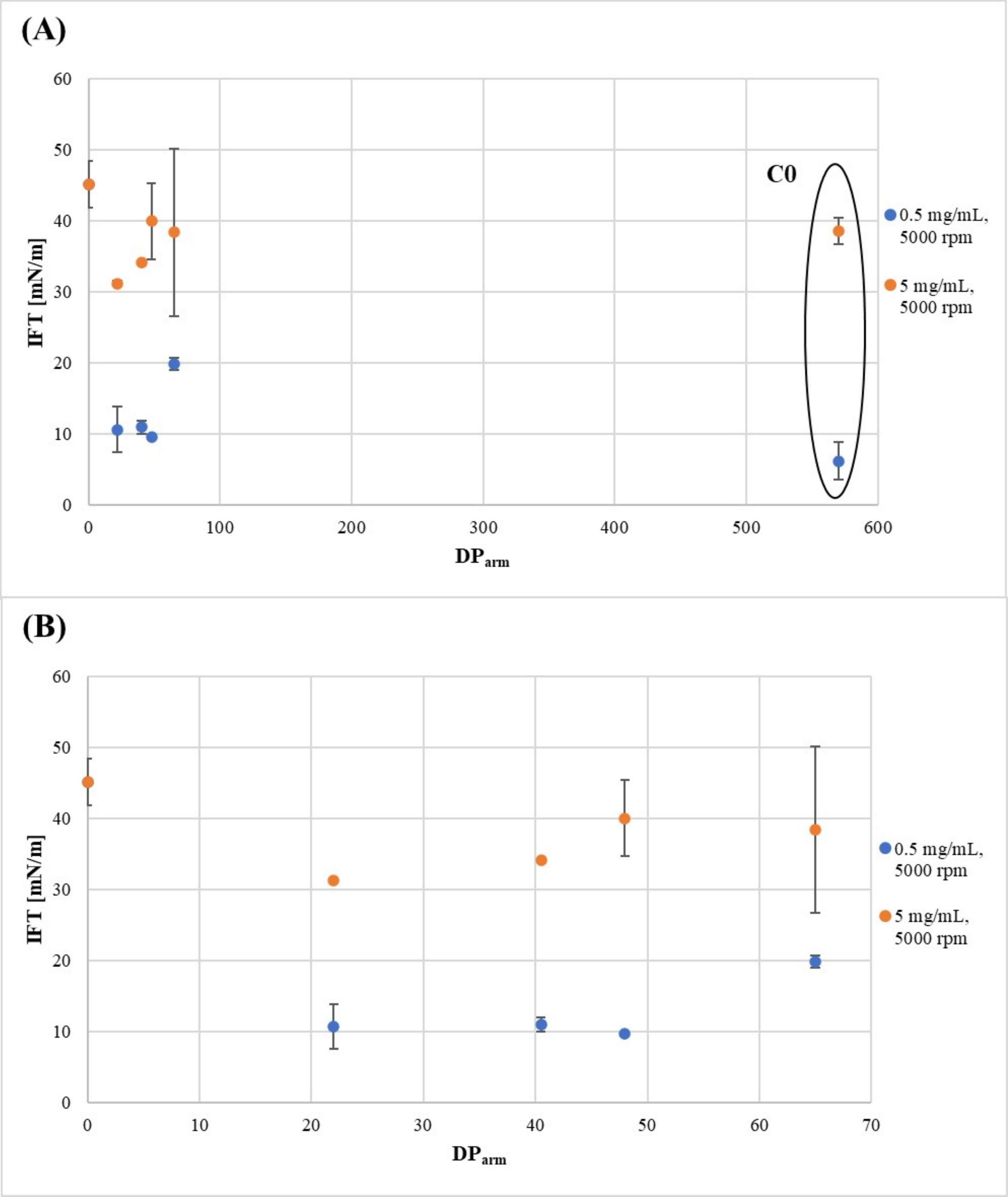

Figure S8. IFT as a function of DP per arm of obtained polymers at a concentration of 0.5 mg/mL and 5 mg/mL (A), a subset of the top graph showing only star-shaped polymers (B).

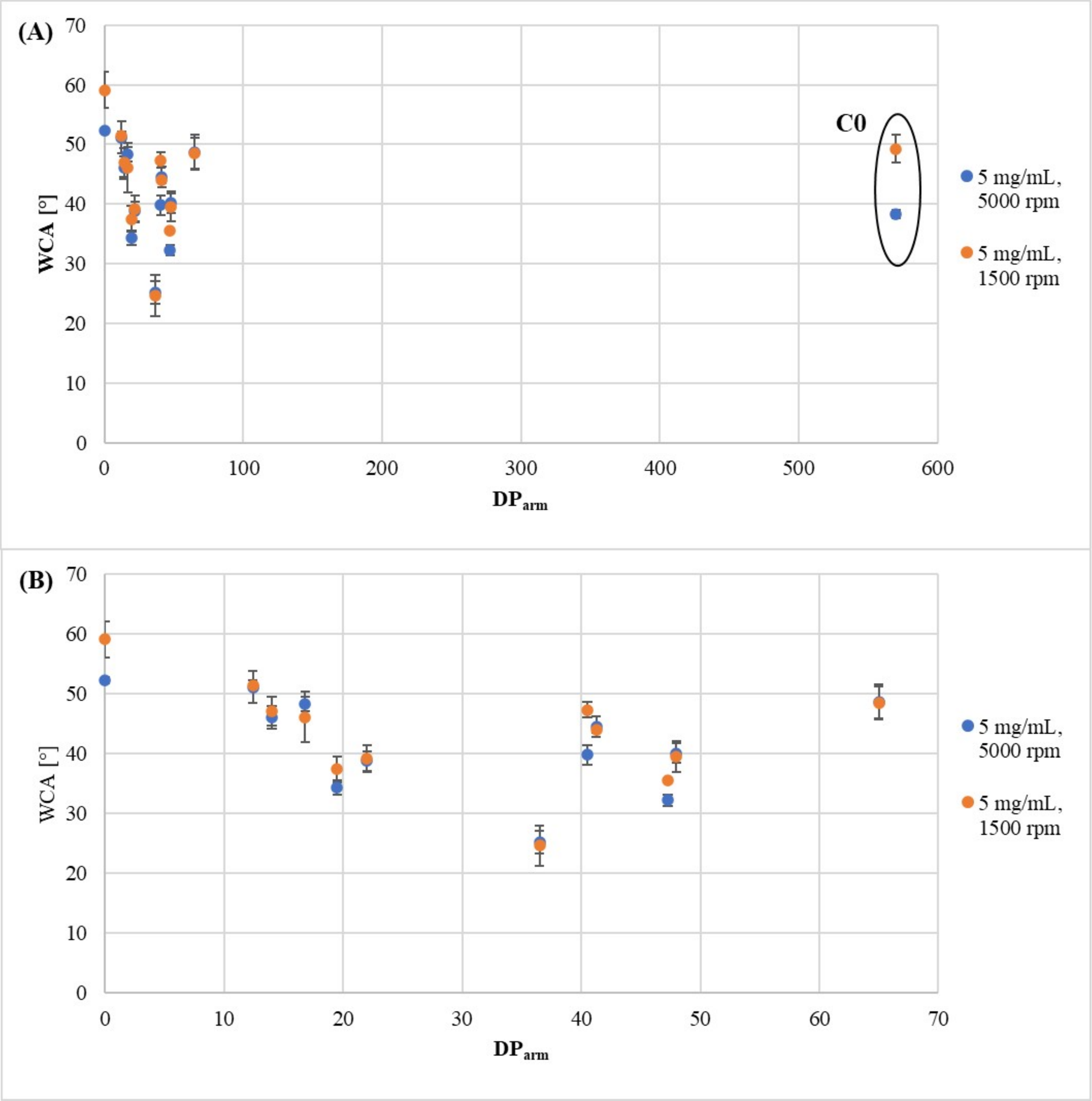

Figure S 9. WCA as a function of DP per arm of obtained polymers at a concentration of 5 mg/mL (A), a subset of the top graph showing only star-polymers (B).

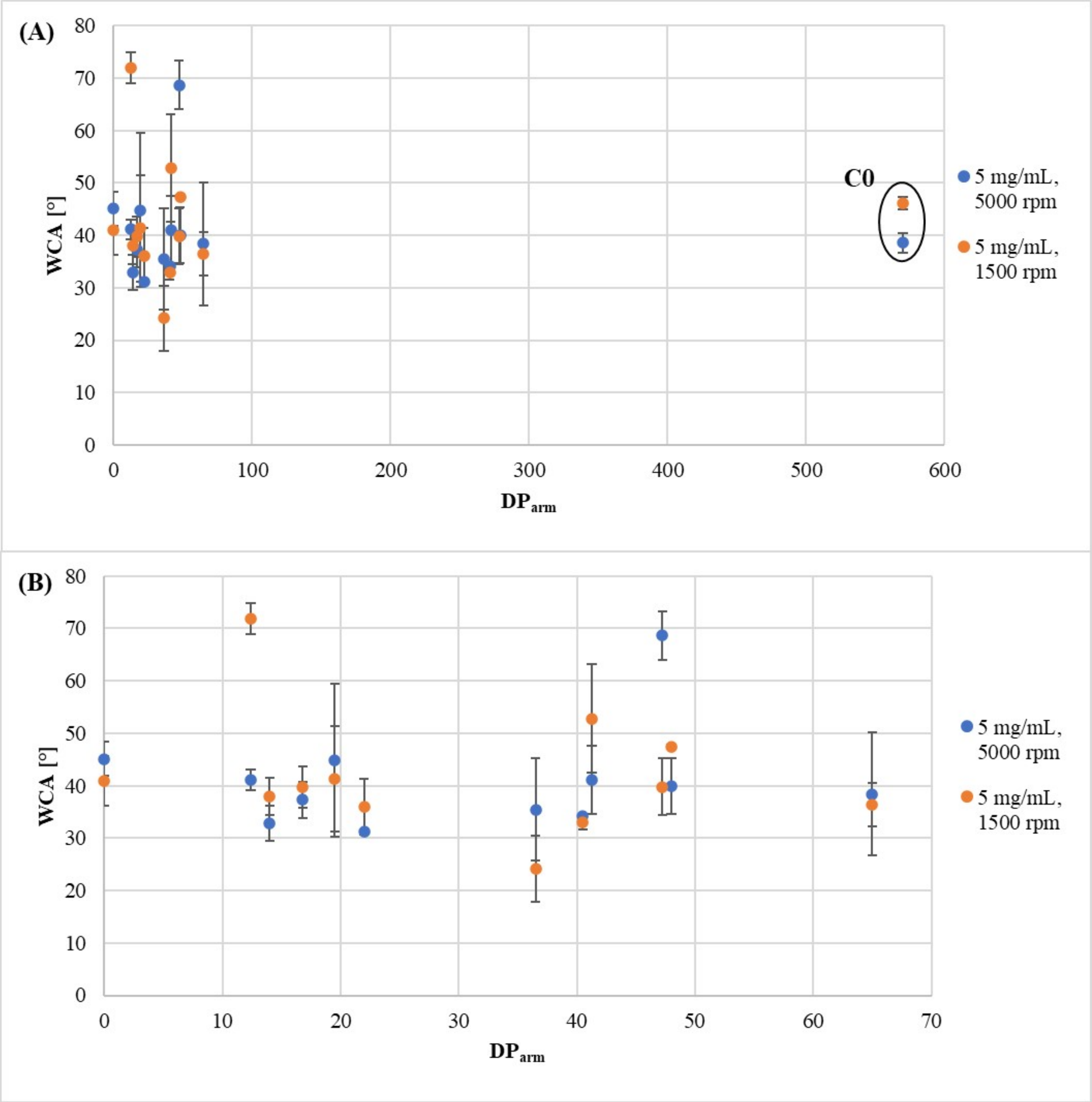

Figure S10. WCA as a function of DP per arm of obtained polymers at a concentration of 5 mg/mL (A), a subset of the top graph showing only star-shaped polymers (B).

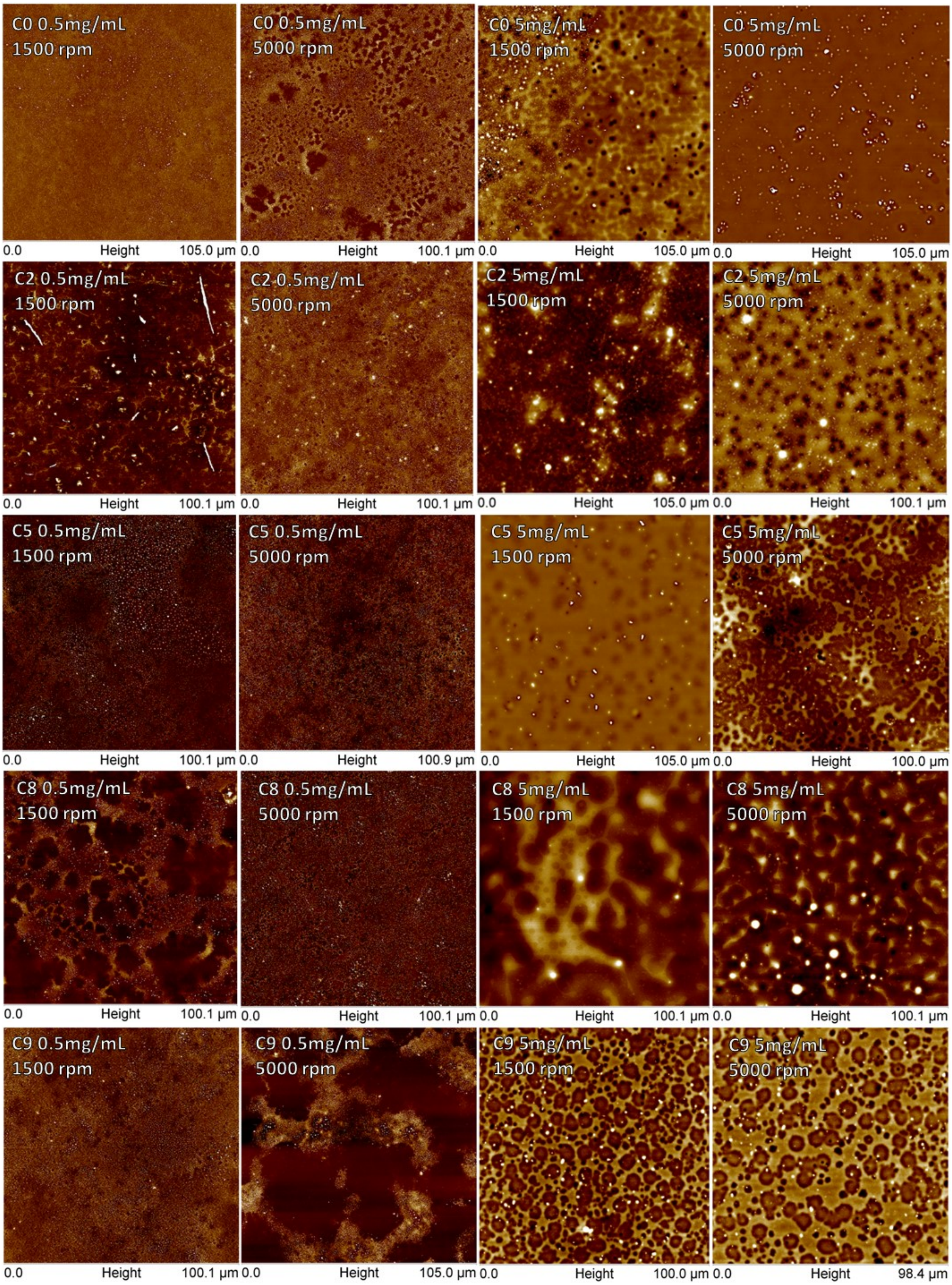

Figure S11. AFM images of the obtained polymeric coatings.

Table S1. Characterization of polymeric coatings

Polymer	DP/DP$_{arm}$	Specification of plate preparation	WCA [°]	R$_a$ [nm]	R$_q$ [nm]	D [nm]
C0	570/-	0.5 mg/mL, 1500 rpm	28.30 ± 3.12	4.00 ± 1.04	6.97 ± 0.83	2.10
C0		0.5 mg/mL, 5000 rpm	22.08 ± 4.80	2.60 ± 0.38	4.12 ± 1.18	1.50
C0		5 mg/mL, 1500 rpm	49.24 ± 2.33	3.70 ± 0.45	6.15 ± 1.2	37.00
C0		5 mg/mL, 5000 rpm	38.30 ± 0.65	1.98 ± 0.53	7.38 ± 4.22	28.00
C2	176/22	0.5 mg/mL, 1500 rpm	27.67 ± 1.12	1.27 ± 0.13	4.60 ± 0.44	1.90
C2		0.5 mg/mL, 5000 rpm	28.17 ± 3.57	1.52 ± 0.10	3.67 ± 1.85	1.40
C2		5 mg/mL, 1500 rpm	39.20 ± 2.20	6.83 ± 1.09	9.52 ± 1.62	36.00
C2		5 mg/mL, 5000 rpm	38.77 ± 1.64	4.75 ± 0.94	11.73 ± 9.42	30.00
C5	324/41	0.5 mg/mL, 1500 rpm	22.85 ± 0.98	3.18 ± 0.86	6.92 ± 2.23	1.40
C5		0.5 mg/mL, 5000 rpm	26.86 ± 1.26	1.94 ± 0.04	3.48 ± 0.22	1.26
C5		5 mg/mL, 1500 rpm	47.35 ± 1.27	3.09 ± 0.58	13.83 ± 4.86	32.00
C5		5 mg/mL, 5000 rpm	39.86 ± 1.65	4.37 ± 1.18	12.17 ± 8.06	27.00
C8	384/48	0.5 mg/mL, 1500 rpm	22.71 ± 1.66	1.95 ± 0.18	4.04 ± 0.37	4.20
C8		0.5 mg/mL, 5000 rpm	28.81 ± 3.34	1.47 ± 0.18	2.87 ± 0.44	1.93
C8		5 mg/mL, 1500 rpm	39.54 ± 2.51	3.32 ± 0.71	6.73 ± 4.86	34.00
C8		5 mg/mL, 5000 rpm	40.15 ± 1.60	2.24 ± 0.01	3.72 ± 0.67	27.00
C9	520/65	0.5 mg/mL, 1500 rpm	24.07 ± 3.70	2.58 ± 0.24	4.57 ± 0.88	6.20
C9		0.5 mg/mL, 5000 rpm	20.34 ± 1.07	2.35 ± 0.28	4.41 ± 0.64	1.18
C9		5 mg/mL, 1500 rpm	48.54 ± 2.66	4.70 ± 0.07	6.18 ± 0.28	31.00
C9		5 mg/mL, 5000 rpm	48.68 ± 2.87	4.80 ± 0.21	7.42 ± 1.20	40.00

Where: R$_a$ - arithmetic mean deviation of the profile from the mean line, R$_q$ - Root Mean Square (RMS), D - coating thickness, ± represent standard deviation from three independent measurements.