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Supplementary Materials

Polymer-assisted biocatalysis: Polyamide 4 microparticles as promising carriers of enzymatic function

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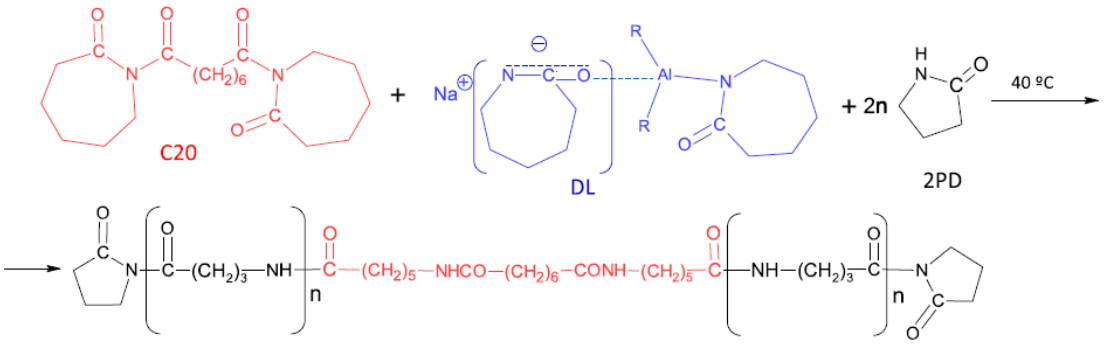

Figure S1. Chemical reactions occurring during AAROP of 2PD to PA4 microparticles: C20 and the chemical structure of the active substance of the C20 activator; DL and the chemical structure of dicaprolactamato-bis-(2-methoxyethoxo)-aluminate (initiator), R = $OCH_2CH_2OCH_3$; 2PD = 2-pyrrolidone.

Viscosity measurements

The intrinsic viscosity measurements were performed with PPD-MIP and PPD-NIP samples in 97% sulfuric acid at a concentration of 0.2 g/dL with a suspended level Ubbelohde viscometer thermostatted at 23ºC. Flow times are recorded as an average of at least 10 runs.

Optical microscopy

Bright field optical microscopy of the PA4, PA4-Fe and PA4-Fe_3O_4 supports and the respective laccase containing samples, i.e., adsorption-immobilized (PA4@iL series) or entrapped (PA4@eL series) was performed evaluating the particles' sizes, roundness, and their distributions were performed in an Olympus BH-2 microscope (Japan) equipped with the Leica Application Suite 4.4 software for image processing. Figure 2S presents the data for the three supports.

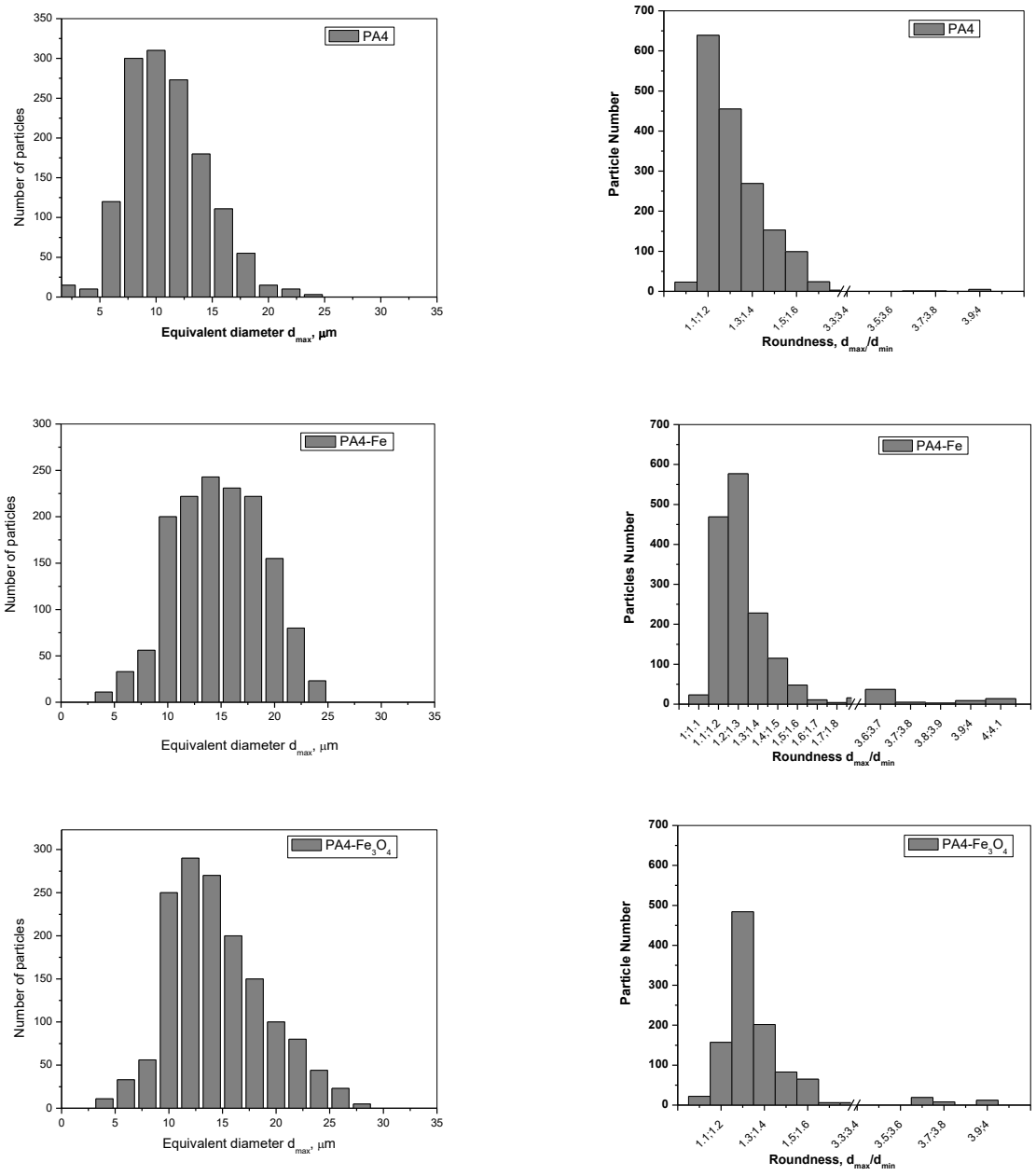

Figure S2. Histograms of the average size (d_{max}) and roundness (d_{max}/d_{min}) distirbutions for PA4 MP supports based on optical microscopy.

Brunauer-Emmet-Teller (BET) analysis.

The BET analysis was performed in a Quantachrome Autosorb IQ automatic gas sorption system using nitrogen gas, outgas time of 1h, bath temperature of 77ºC and equilibrium time of 1 h. The amount of the samples was in the 300-400 mg range. S_{BET} = surface area; V_{total} = pore volume; σ_{ave} = average pore size

Table S1. Data from BET for empty PA4 supports.

Sample	S_{BET} (m^2/g)	V_{total}(cm^3/g)	σ_{ave} (Å)
PA4	2.766	0.0112	31.69
PA4-Fe	2.052	0.004	85.29
PA4-Fe_3O_4	2.542	0.008	41.60

Z-potential measurements

The electric charge of the PPD-MIP and PPD-NIP systems was evaluated by zeta potential determined at pH 4.0, pH 5.0 (both phosphate buffer 0.01 M) and pH 7 (deionized water), at 25.0 ± 0.1 °C. Measurements were performed with a microelectrophoresis cell (DLS Nanosizer, Malvern) in a Zetasizer Nano ZS apparatus of Malvern Instruments. The applied voltage was 200 V and each mean value consisted of 100 recordings.

Table S2. Z-potential values of empty particulate PA4-based supports.

Sample designation	Z potential, eV		
	pH 7	pH 5	pH 4
PA4	-35.8	-16.2	- 4.9
PA4-Fe	-35.8	-12.9	+1.5
PA4-Fe_3O_4	-33.6	-14.5	-3.0

Table S3. Consolidated DSC data from an initial heating scan, subsequent cooling scan and a second heating scan at 10 deg/min.

Sample designation	T^1_m ^oC	ΔH^1_m J/g	T_c, ^oC	$-\Delta H_c$ J/g	T^2_m ^oC	ΔH^2_m J/g
PA4	235.0	78.1	197.8	36.9	236.8	13.4
PA4-Fe	247.5	60.7	183.7	40.8	247.5	27.4
PA4-Fe_3O_4	240.5	63.8	187.0	30.8	243.1	20.0
PA4-i*L*	262.3	45.8	211.6	28.4	247.5	10.0
PA4-Fe-i*L*	260.4	55.2	214.0	20.3	245.9	10.3
PA4-Fe_3O_4-i*L*	261.2	59.7	210.1	29.0	248.9	10,1
PA4-e*L*	245.8	64.3	174.2	8.7	225.1	5.6
PA4-Fe-e*L*	249.4	61.8	188.9	10.0	234.3	5.7
PA4-Fe_3O_4-e*L*	224.1	72.23	172.9	11.7	228.9	2.5

Notes: T^1_m and ΔH^1_m – melting temperature and enthalpy during the first scan; T_c and ΔH_c – crystallization temperature and enthalpy during the cooling scan; T^2_m and ΔH^2_m – melting temperature and enthalpy during the second scan.

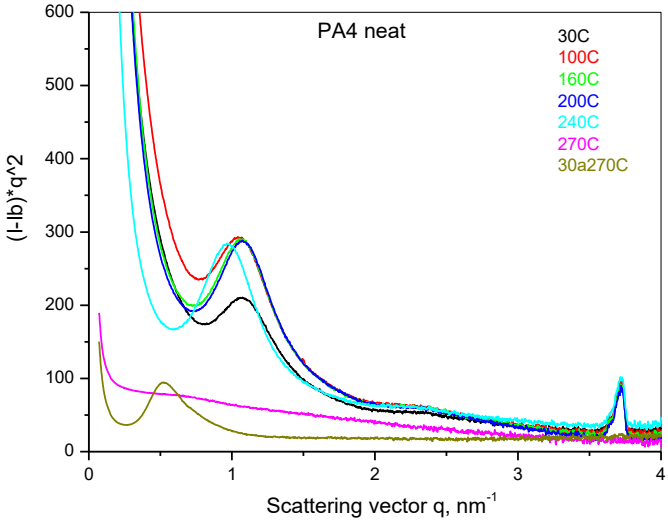

Figure S3. Disappearance of the scattering peak at q = 3.73 nm-1 in the SAXS patterns after melting and recrystallization of PA4 MP support – see the curves at 270C and 30a270C.

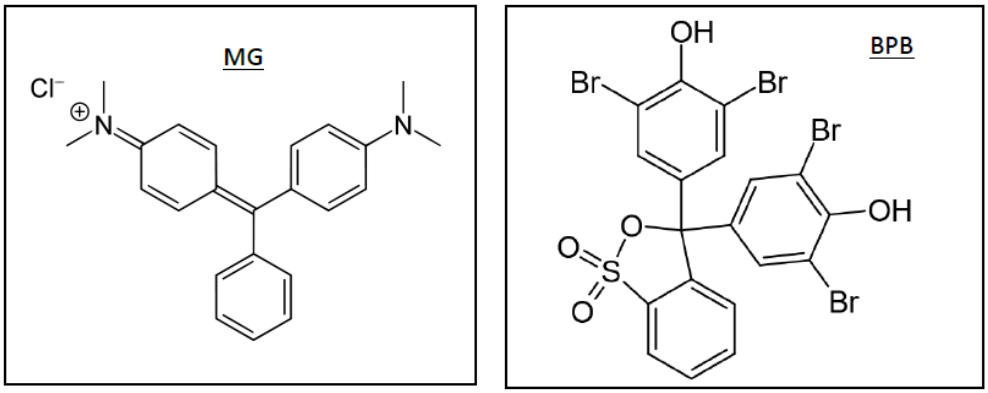

Figure S4. Structures of the dyes used in the discoloration studies with PA4@iL and PA4@eL laccase conjugates: MG = malachite green; BPB = bromophenol blue.

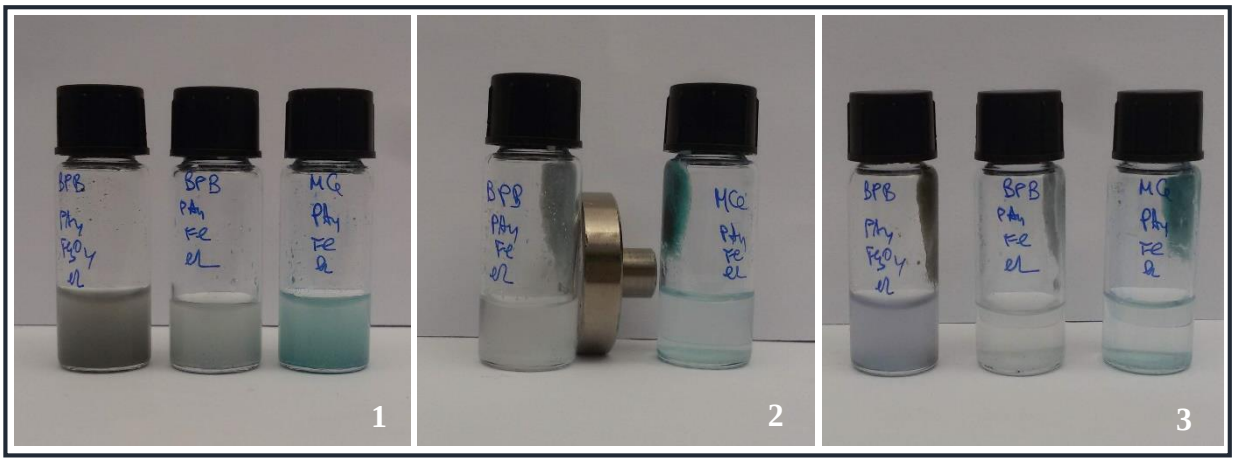

Figure S5. | PA4-Fe-eL sample fast removal from DDW suspension: 1 – Conjugate suspension in water; 2, 3 - phases of conjugate separation applying a constant magnet (BPB-bromphenol blue; MG-malachite green).