ELECTRONIC SUPPORTING INFORMATION

Enzymatic Approach for the Synthesis of Biobased Aromatic-aliphatic Oligo-/Polyesters

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Materials. Methyl vanillate (≥98%), syringic acid (≥98%), anhydrous N,N-dimethyl formamide (DMF, 99.8%), potassium carbonate (K_2CO_3, ≥99%,), sodium bicarbonate ($NaHCO_3$, 99.5%,), sodium sulfate (reagent grade, $NaSO_4$), sodium hydride (60 % dispersion in mineral oil, NaH) were purchased from Sigma-Aldrich and used as received. 2-bromoethanol (95%) obtained from Sigma-Aldrich were freshly distilled at 65 ^oC under reduced pressure and kept under nitrogen until used. Absolute ethanol (EtOH) and absolute methanol (MeOH) were obtained from Biosolve Chemicals, and used without further purification. Ethyl acetate (EtOAc, ChromAR HPLC), dichloromethane (DCM, AR amylene stabilized) were obtained from Macron and used as received. Hydrochloride acid (HCl, 37-38%) was obtained from Boom. Deuterated chloroform ($CDCl_3$, 99.8 atom% D) was purchased from Sigma-Aldrich and used as received

Preparation of methyl 4-(2-hydroxyethoxy)-3-methoxybenzoate. Methyl vanillate (10.50 g, 57.66 mmol) was dissolved in anhydrous N,N-dimethyl formamide (48 mL) and 2-bromoethanol (15.00 g, 120 mmol) was added slowly to the solution under nitrogen atmosphere. The reaction mixture was strongly stirred for 5 min, followed by adding potassium carbonate (23.80 g, 172.2 mmol). The reaction mixture was heated to 70 ^oC and stirred under nitrogen atmosphere. After 24 h reaction time, the mixture was cooled down and ethyl acetate (100 mL) and 1N hydrochloride acid aqueous solution (100 mL) were added to the mixture. The organic phase was washed with water (2 x 80 mL) followed by saturated sodium bicarbonate solution (2 x 80 mL) and brine (2 x 80 mL). The organic phase was separated, dried over sodium sulfate and concentrated in vacuum to obtain a crude methyl 4-(2-hydroxyethoxy)-3-methoxybenzoate product (7.52 g, 57.7%). The product was purified by column chromatography from dichloromethane/ethyl acetate (1:1) and the pure compound was obtained as a pale colored solid.

TLC (DCM/EtOAc, 1/1): R_f = 0.46; ^{1}H NMR (400 MHz, chloroform-*d*): δ 3.90 (3H, s), 3.92 (3H, s), 3.99 (2H, t, *J* =4.39 Hz), 4.10 (2H, t, *J* =4.69 Hz), 6.92 (2H, d, *J* =8.40 Hz), 7.56 (1H, d, *J* =1.77 Hz), 7.60 (1H, dd, *J* = 8.40, 1.90 Hz) ppm; ^{13}C NMR (100.6 MHz, chloroform-*d*):δ 52.18 (C16), 56.10 (C8), 61.30 (C14), 70.87 (C13), 112.57 (C1), 112.73 (C4), 123.09 (C5), 123.54 (C6), 144.00 (C3), 152.99 (C2), 166.51 (C9) ppm; M_p (DSC): 77.2 ^oC.

Preparation of methyl 4-(2-hydroxyethoxy)-3,5-dimethoxybenzoate. Syringic acid (4.91 g, 24.76 mmol) was dissolved in absolute methanol (80 mL) and catalytic amount of concentrated sulfuric acid was added, and purged with nitrogen. The reaction mixture was heated to 65 ^{o}C and stirred under nitrogen atmosphere. After 12 h reaction time the system was cooled down and concentrated under vaucuum, followed by dissolving in ethyl acetate and was washed with saturated sodium bicarbonate (2 x 80 mL) solution, distilled water (80 mL) and brine (80 mL). The organic phase was collected and dried over sodium sulfate. The filtered solution was concentrated to dryness with a yield of 93%. The synthetized and purified methyl syringate (2.12 g, 9.97 mmol) was dissolved in anhydrous *N*, *N*-dimethyl formamide (20 mL), cooled down with ice water under continuous stirring. Then sodium hydride (60%, 410 mg, 10.25 mmol) was added and the mixture was stirred for addition 20 min at this low temperature, followed by the slow addition of 2-bromoethanol (3.12 g, 24.97 mmol). The reaction mixture was heated to 80 ^{o}C and stirred under nitrogen atmosphere. After the 2 h reaction time, the mixture was cooled down to room temperature, was quenched with distilled water (18 mL) followed by extraction with ethyl acetate (60 mL). The collected organic phase was washed with brine (20 mL) and dried over sodium sulfate, filtered and concentrated. The product was further purified by column chromatography from dichloromethane/ethyl acetate mixture (1/1) and the pure compound was obtained as a pale colored solid.

TLC (DCM/EtOAc, 1/1): R_f = 0.66; ^{1}H NMR (400 MHz, chloroform-*d*): δ 3.72 (2H, t, *J* =4.52 Hz), 3.90 (6H, *s*), 3.93 (3H, s), 4.17 (2H, t, *J* =4.69 Hz), 7.31 (2H, s) ppm; ^{13}C NMR (100.6 MHz, chloroform-*d*):δ 52.45 (C14), 56.39 (C8,C10), 61.50 (C17), 75.59 (C16), 106.75 (C4,C6), 125.78 (C5), 144.12 (C2), 153.10 (C1,C3), 166.97 (C11) ppm; M_p (DSC): 83.4 ^{o}C.

Table S1 Synthetic parameters and polymerization data of conventional and CALB-catalyzed polycondensation reactions of methyl 4-(2-hydroxyethoxy)-3-methoxybenzoate.

			NMR[e]	GPC[f]			MALDI-ToF MS[g]		
Entry	catalyst	Yield[d](%)	M_n (g/mol)	M_n (g/mol)	M_w (g/mol)	*Đ*	M_n (g/mol)	M_w (g/mol)	*Đ*
S1	CALB[a]	60	1230	1070	1150	1.08	990	1030	1.04
S2	CALB[b]	57	1590	1210	1310	1.08	920	950	1.04
S3	Sb_2O_3[c]	81	NA	6640	11080	1.67	2500	3000	1.20

Polymerization conditions: [a)] constant temperature under nitrogen atmosphere, 20wt% CALB; [b)] temperature varied two stage method under dynamic vacuum, 20wt% CALB; [c)]monomer melting and polymerization under dynamic vacuum (10 h) at 220 ^{o}C, 2mol% Sb_2O_3; [d)]isolated yield after precipitation in methanol; [e)]calculated from ^{1}H NMR spectra in $CDCl_3$/TFA-*d* mixture; [f)]determined from GPC analysis in $CHCl_3$ (6v/v% HFIP) by conventional calibration method; [g)]determined from MALDI-ToF MS spectra (dithranol matrix).

Table S2 Thermal and crystalline properties of oligo-/poly(ethylene vanillate)s.

	DSC[a]						TGA[b]	
Entry	T_g (°C)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (°C)	ΔH_m (J/g)	χ_c (%)	$T_{d5\%}$ (°C)	$T_{d(max)}$ (°C)	Y_c (500 °C) (%)
S1	68	198.0	15.960	239	65.24	95.9		422	4.2
S2	80	204	5.636	254	62.47	91.9		422	4.3
S3	81	207	19.740	252	63.34	93.1		420	4.2

[a)]determined from DSC analysis (T_g is around 74 °C and T_m is between 239 and 264 °C[1, 2]; ΔH_m^0 is 68 J/g [1]); [b)]determined from TGA analysis ($T_{d(max)}$ is around 417 °C[2]).

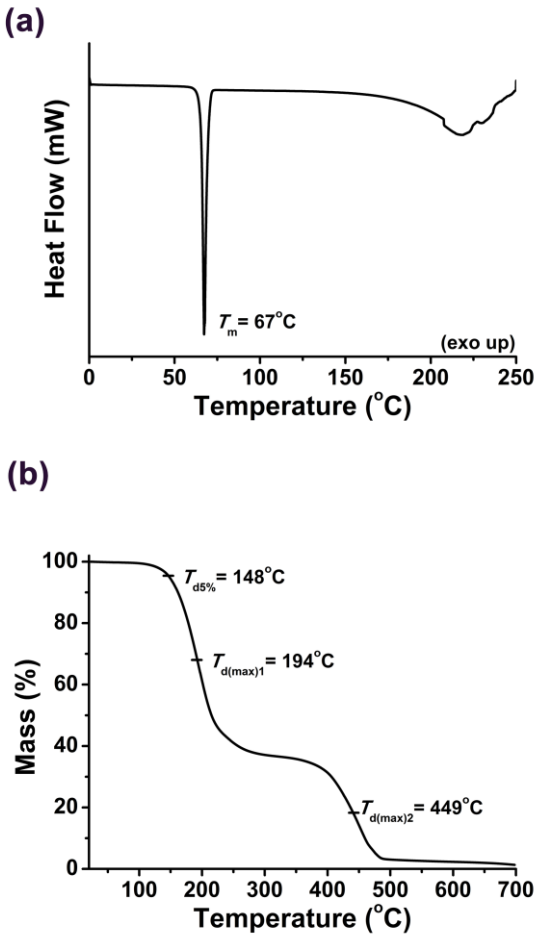

Figure S1 (a) DSC thermogram (heating cycle) and (b) TGA trace of 4-(2-hydroxyethoxy)benzoic methyl ester.

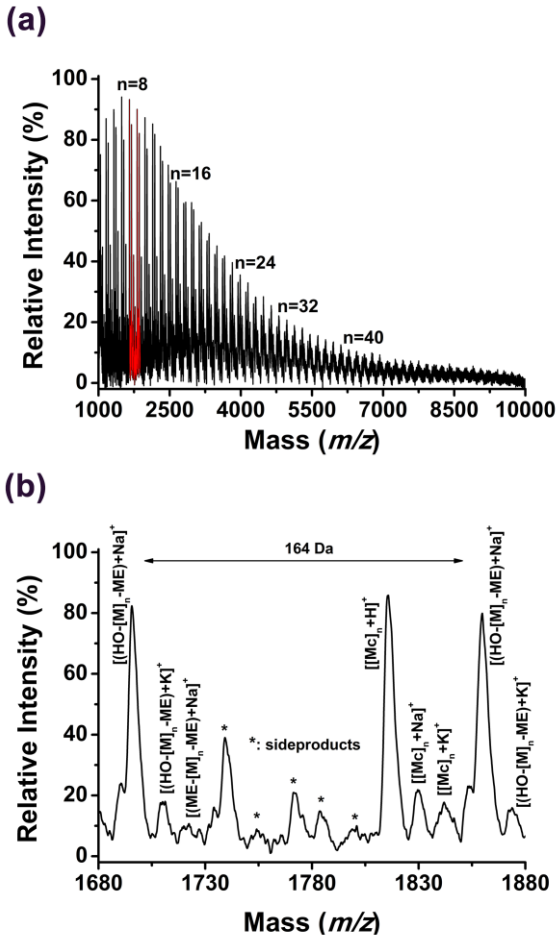

Figure S2 (a) MALDI-ToF linear mass spectrum of poly(2-hydroxyetloxy benzoate) polymer and (b) magnification of a set of peaks of the MALDI-ToF MS spectrum, repeating set of peaks starting with HO-[M]-ME/Na^+, where *M* = 164 Da (HEBA) (entry 7 of Table 1).

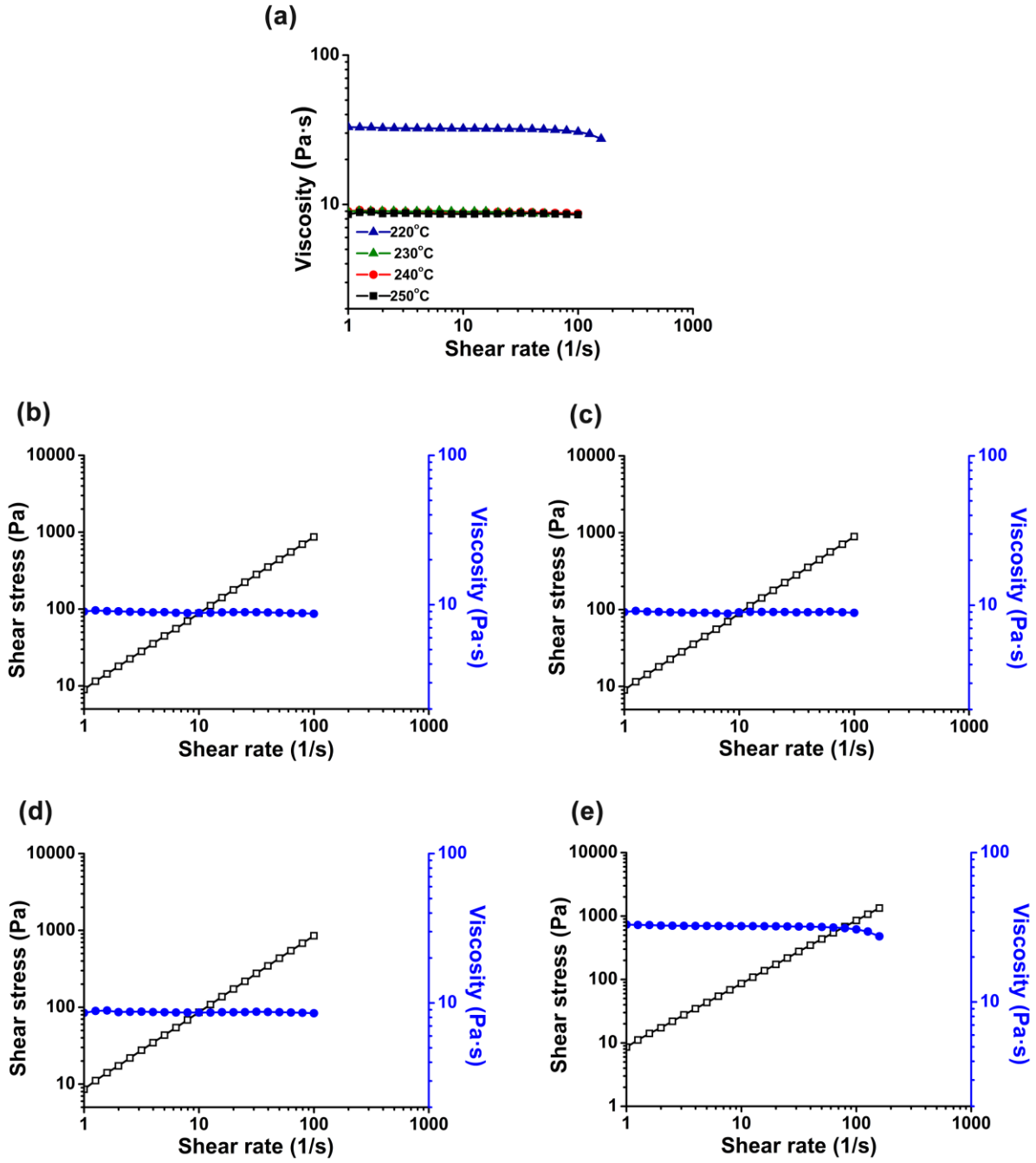

Figure S3 (a) Effect of temperature on the flow test of obtained oligo(2-hydroxyethoxy benzoate) sample (entry 5 of Table 1) at different temperatures and the shear stress *vs.* shear rate and viscosity *vs.* shear rate curves at: (b) 220 °C, (c) 230 °C, (d) 240 °C and (e) 250 °C.

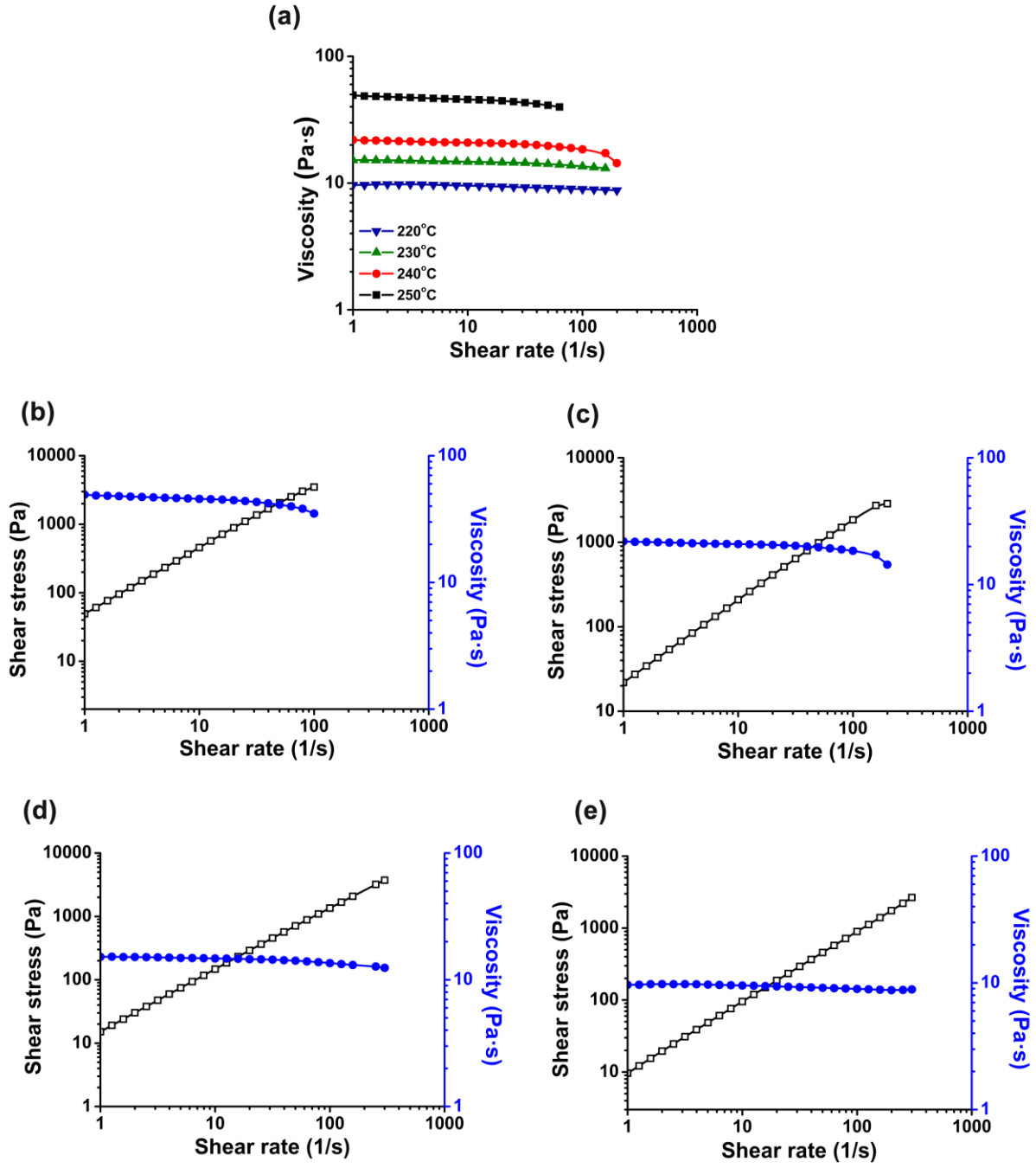

Figure S4 (a) Effect of temperature on the flow test of obtained low molecular weight poly(2-hydroxyethoxy benzoate) sample (entry 7 of Table 1) at different temperatures and the shear stress *vs.* shear rate and viscosity *vs.* shear rate curves at: (b) 220 °C, (c) 230 °C, (d) 240 °C and (e) 250 °C.

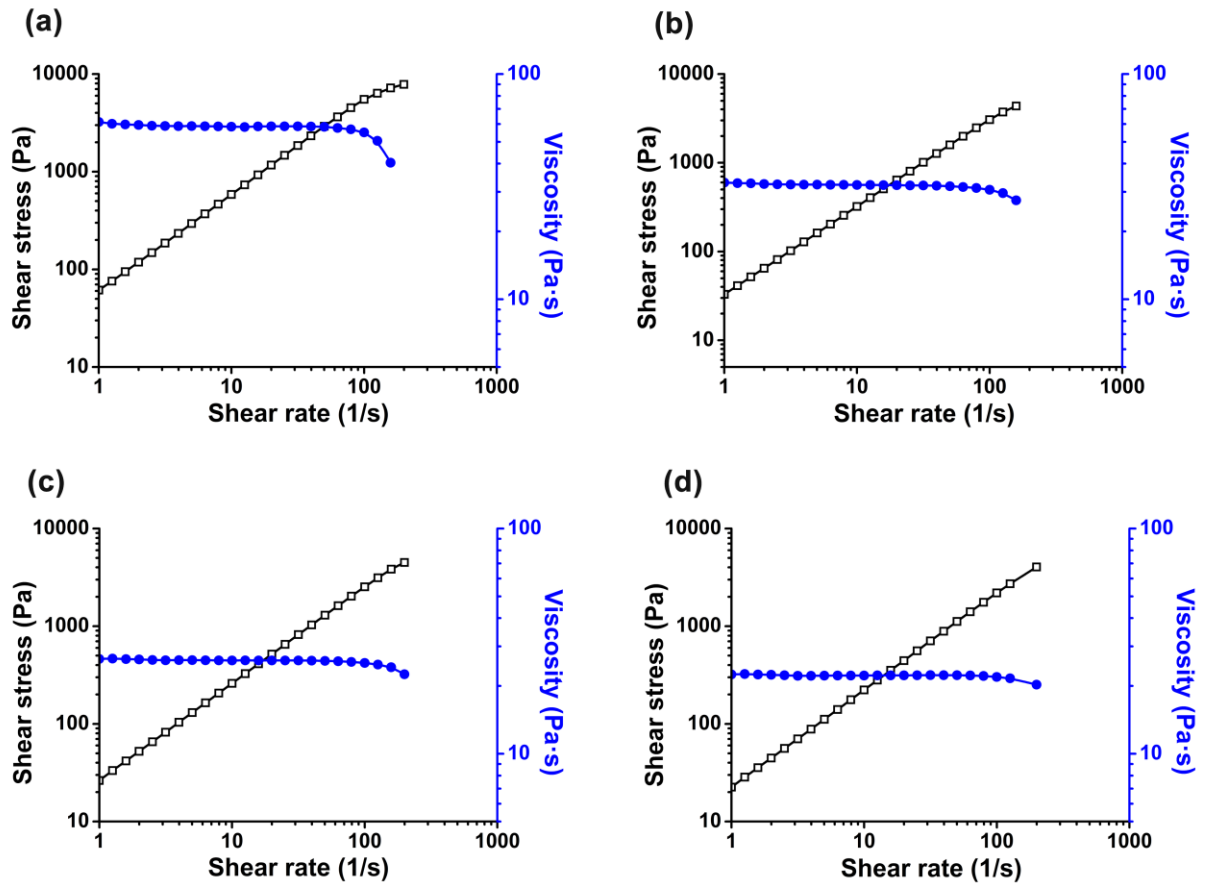

Figure S5 The shear stress *vs.* shear rate and viscosity *vs.* shear rate curves of obtained poly(2-hydroxyethoxy benzoate) sample (entry 9 of Table 1) at different temperatures of: (a) 220 °C, (b) 230 °C, (c) 240 °C and (d) 250 °C.

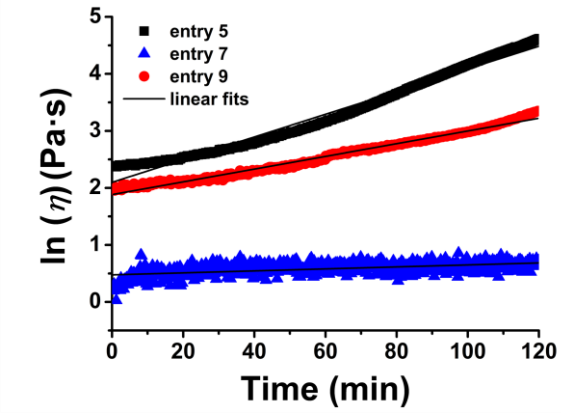

Figure S6 Time sweep curves and their linear fittings of different molecular weight samples (entry 5, 7 and 9 of Table 1) at 290 °C.

References and Notes

1. C. Gioia, M. B. Banella, P. Marchese, M. Vannini, M. Colonna and A. Celli, *Polymer Chemistry*, 2016, **7**, 5396-5406.
2. L. Mialon, R. Vanderhenst, A. G. Pemba and S. A. Miller, *Macromolecular Rapid Communications*, 2011, **32**, 1386-1392.