Supporting Information (SI)

Effect of Methoxy Substituent Position on Thermal Properties and Solvent Resistance of Lignin-Inspired Poly(dimethoxyphenyl methacrylate)s

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Materials and Experimental Methods

Synthesis and characterization of 2,3-; 3,5-; 2,4-; and 2,6-dimethoxyphenyl methacrylates (2,3D; 3,5D; 2,4D; and 2,6D).

Dimethoxyphenyl methacrylate monomers were synthesized using an adapted version of a procedure described in the literature.[1] 2,3-dimethoxyphenol (Acros Organics, 99%), 3,5-dimethoxyphenol (Acros Organics, 97%), 2,4-dimethoxyphenol (Ark Pharm, 98%), or 2,6-dimethoxyphenol (Fisher Scientific, 99%), and triethylamine (1.2 mol eq, Fisher, 99%) were dissolved in dichloromethane (DCM, Fisher Scientific) in a three-neck round-bottom flask. The flask was immersed in an ice-water bath, and the mixture inside was sparged with argon for 15 min. A solution of methacryloyl chloride (1.2 mol eq, Alfa Aesar, 97%) in DCM was added dropwise to the flask using a constant pressure dropper. The reaction proceeded overnight until a conversion of 70-90 mol% was achieved. The white precipitant was removed by vacuum filtration, and the soluble product in DCM was washed consecutively with solutions of saturated sodium bicarbonate, 1.0 M NaOH, 0.5 M NaOH, 1.0 M HCl, saturated NaCl, and deionized water. After removing the solvent by rotary evaporation, the monomer was further purified by flash chromatography using silica gel (Standard Grade, 230 × 400 mesh, 60 Å) with an eluent (ethyl acetate/hexanes with ethyl acetate volume percent gradually increasing from 0% to 10%). In the column purification of 2,6D, an eluent mixture of hexanes and DCM was used, with a step change of DCM percentage at 30 vol% [3 column volumes (CV)], 50 vol% (3 CV), and 70 vol% (10 CV). ^{1}H NMR δ ppm ($CDCl_3$, 600 MHz) for **2,3D:** 7.03 (1H, t), 6.82 (1H, d), 6.71 (1H, d), 6.37 (1H, s), 5.76 (1H, s), 3.88 (3H, s), 3.82 (3H, s), 2.08 (3H, s); **3,5D:** 6.35 (1H, t), 6.33 (1H, s), 6.30 (2H, d), 5.75 (1H, s), 3.78 (6H, s), 2.05 (3H, s); **2,4D:** 6.96 (1H, d), 6.54 (1H, d), 6.45

(1H, m), 6.35 (1H, s), 5.73 (1H, s), 3.80 (6H, s), 2.06 (3H, s); and **2,6D:** 7.14 (1H, t), 6.62 (2H, d), 6.39 (1H, s), 5.75 (1H, s), 3.81 (6H, s), 2.08 (3H, s).

Synthesis and characterization of poly(dimethoxyphenyl methacrylate)s [P(2,3D), P(3,5D), P(2,4D), P(2,6D-*co*-3,5D), and P(2,6D-*co*-2,4D)]

The homopolymers were synthesized by reversible addition-fragmentation chain-transfer (RAFT) polymerization, following a procedure reported in the literature.[2] 2,2′-Azobisisobutyronitrile (AIBN, Sigma-Aldrich, 98%) was recrystallized twice from methanol. The chain transfer agent, 2-cyano-2-propyl benzodithioate (CPB, STREM Chemicals, 97%), was used as received. The polymerization solvent, anisole (Sigma-Aldrich, ≥99.7%) with 5 wt% N,N-dimethylformamide (DMF, Sigma-Aldrich, ≥99.9%) as an internal standard, was prepared in advance and stored on molecular sieves to minimize water uptake. At a predetermined ratio (see Table S1 for details), the monomer, CPB, and AIBN were dissolved in the polymerization solvent and transferred to a pressure vessel. The reaction mixture was degassed by three freeze-pump-thaw cycles, backfilled with argon to a pressure of 2-3 psi, sealed with a stopcock, and immersed in a pre-heated oil bath (72 °C) with vigorous stirring. After a predetermined time (see Table S1 for details), the reaction was quenched by immersing the pressure vessel in liquid nitrogen. Tetrahydrofuran (THF) or DCM was added to the mixture, and the polymer was purified by precipitating into excess hexanes at least two times to ensure that no monomer was remaining [confirmed by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy]. Note that the synthesis and molecular characterization of the three P(2,6D) homopolymers were reported in previous work.[3] For the synthesis of the statistical copolymers, the same procedure was

employed as detailed above, except that a mixture of 2,6D/2,4D or 2,6D/3,5D was added instead of a single monomer.

P(2,3D): ^{1}H NMR δ ppm ($CDCl_3$, 600 MHz): 7.02-6.59 (3H, br), 3.93-3.54 (6H, br), 2.75-1.93 (2H, many br), 1.40-1.11 (3H, br).

P(2,4D): ^{1}H NMR δ ppm ($CDCl_3$, 600 MHz): 7.15-6.93 (1H, br), 6.52-6.17 (2H, br), 3.83-3.50 (6H, br), 2.75-1.21 (5H, many br).

P(3,5D): ^{1}H NMR δ ppm ($CDCl_3$, 600 MHz): 6.36-6.16 (3H, br), 3.70-3.50 (6H, br), 2.49-1.19 (5H, many br).

P(2,6D-*co*-3,5D): ^{1}H NMR δ ppm ($CDCl_3$, 600 MHz): 7.15-6.84 (1H/2,6D, br), 6.65-6.05 (2H/2,6D + 3H/3,5D, br), 3.94-3.30 (6H/2,6D + 6H/3,5D), 2.99-1.18 (5H/2,6D + 5H/3,5D, many br). The 2,6D content was determined *via* the characteristic aromatic proton peak from P(2,6D) at 7.15-6.84 ppm. Monomer feed composition (mol/mol): $f_{2,6D}$ = 0.65, $f_{3,5D}$ = 0.35. Polymer composition (mol/mol): $F_{2,6D}$ = 0.64, $F_{3,5D}$ = 0.36.

P(2,6D-*co*-2,4D): ^{1}H NMR δ ppm ($CDCl_3$, 600 MHz): 7.18-6.85 (1H/2,6D + 1H/2,4D, br), 6.67-6.14 (2H/2,6D + 2H/2,4D, br), 3.94-3.30 (6H/2,6D + 6H/2,4D), 2.99-1.18 (5H/2,6D + 5H/2,4D, many br). The broad peaks (triplets) at 6.67-6.14 ppm were composed of characteristic aromatic proton peak from P(2,6D) at 6.67-6.38 ppm (single) and characteristic aromatic proton peaks from P(2,4D) at 6.52-6.14 ppm (double). After de-convolution of the three broad peaks, the

2,6D content was calculated *via* the characteristic aromatic proton peak from P(2,6D) at 6.67-6.38 ppm. Monomer feed composition (mol/mol): $f_{2,6D} = 0.44$, $f_{2,4D} = 0.56$. Polymer composition (mol/mol): $F_{2,6D} = 0.41$, $F_{2,4D} = 0.59$.

Characterization of polymers

The monomer to polymer conversion was determined from ^{1}H NMR spectroscopy using $CDCl_3$ (0.03 v/v% TMS) as the solvent on a Bruker NMR spectrometer AVIII, 600 MHz. The ratio of the two monomers in the statistical copolymers also was determined *via* ^{1}H NMR spectroscopy using the characteristic peaks for each component.

The number-average molecular weight (M_n), weight-average molecular weight (M_w), and dispersity ($Đ$) were obtained using a Viscotek VE2001 size exclusion chromatography (SEC) instrument with THF as the eluent (1.0 mL/min), with polystyrene standards (1.78-205 kg/mol) as a reference.

Glass transition temperatures (T_g's) of all polymers were determined using a differential scanning calorimeter (DSC, Discovery Series, TA Instruments). The DSC was calibrated using an indium standard. Polymer powder (3-6 mg) was loaded into an aluminum pan and hermetically sealed in air. Three heating and cooling cycles were performed at a rate of 5 °C/min under continuous N_2 flow (50 mL/min), with a temperature ramp range of 40-200 °C for P(2,3D), 20-160 °C for P(3,5D), 60-190 °C for P(2,4D), 140-250 °C for P(2,6D),[3] and 60-200 °C for P(2,6D-*co*-3,5D) and P(2,6D-*co*-2,4D). There were no significant changes between the second and the third

heating cycles, and the T_g was determined as the midpoint of the inflection in the second heating. To approximate the dependence of T_g on M_n, the Flory-Fox equation[4] was employed:

$$T_g = T_{g,\infty} - \frac{K}{M_n}, \quad \text{(S1)}$$

in which M_n is the molecular weight of the polymer, K is the empirical Flory-Fox coefficient, and $T_{g,\infty}$ is the T_g extrapolated to infinite molecular weight.

The thermal degradation properties of the polymers were characterized using thermogravimetric analysis (TGA, Discovery Series, TA Instruments). 4-6 mg of each polymer (powdered) were loaded into 100 μL platinum pans and heated under continuous airflow (50 mL/min sample purge, 20 mL/min balance purge). Samples were initially heated at 20 °C/min to 110 °C and annealed for 15 min to remove possible residual water. The samples then were cooled at 10 °C/min to 50 °C, held for 1 min, and heated at 10 °C/min to 600 °C. The characteristic degradation temperatures reported herein are the temperatures at which the weight of polymer was reduced by 5% ($T_{5\%}$) and the peak degradation temperature (T_p, the temperature at the maximum of the first derivative with respect to temperature), after normalizing the data to the mass at 110 °C.

The solvent resistance of the polymers was probed by solvent vapor annealing (SVA) experiments on thin polymer films, following a procedure described in the literature.[5] Solutions of 2 wt% polymer in DCM were prepared and cast onto UVO cleaned silicon wafers using a homebuilt flow coater.[5] The flow coater was operated at a velocity of 11-14 mm/s, acceleration of 0.4 mm/s^2, gap height of 70 μm, and blade width of 15 mm. The film thickness in all cases herein was greater than 100 nm to remove dependence of the swelling behavior on the initial film

thickness.[6] Two commonly used organic solvents, THF and chloroform ($CHCl_3$), were employed to demonstrate the differences in solvent swelling between the polymers. Solvent-rich vapor was generated by bubbling nitrogen (N_2) through either THF or $CHCl_3$, and the partial pressure (p) of solvent vapor was adjusted by controlling the relative flow rates of the vapor stream and a second pure N_2 stream. The total flow rate was kept constant throughout the process at 26 mL/min. The film thickness was measured *in situ* during the swelling process using a spectral reflectometer (Filmetrics, Inc. F20-UV) after correcting for the refractive indices of the solvent-swollen films. Average laboratory temperatures of 25.5 °C and 26.5 °C for the THF and $CHCl_3$ SVA experiments, respectively, were used to calculate the saturated partial pressure (p_{sat}) of the solvent vapor, using the Antoine equation.[7] The SVA experiment in THF was performed first at a p/p_{sat} value of 0.85. When the film thickness equilibrated, p/p_{sat} was reduced to a p/p_{sat} value of 0.77. The SVA experiment was stopped after the film thickness equilibrated at this second partial pressure. For the SVA experiment in $CHCl_3$, dewetting of all polymer films, except P(2,6D), was noted at p/p_{sat} values of 0.90, 0.82, and 0.71. Therefore, the p/p_{sat} in the $CHCl_3$ SVA experiment initially was set to a value of 0.67, and the p/p_{sat} was lowered to a value of 0.59 once the film thickness became invariant at the first partial pressure.

Table S1: Polymerization details and polymer characteristics

Polymer[a]	$[M]_0/[CTA]_0$[b]	$[I]_0/[CTA]_0$[c]	t (h)	x[d]	$M_{n,calc}$[e] (kg/mol)	$M_{n,SEC}$[f] (kg/mol)	$M_{w,SEC}$[f] (kg/mol)	$Đ$[f]
P(3,5D)-38k	225	0.1	7	82%	41.0	38.1	46.2	1.21
P(3,5D)-33k	225	0.1	4	68%	34.0	32.8	41.7	1.27
P(3,5D)-23k	225	0.1	2	40%	20.0	22.5	30.7	1.36
P(2,3D)-20k	225	0.1	8	60%	30.0	19.7	27.6	1.40
P(2,3D)-16k	228	0.1	6	51%	25.8	16.1	24.1	1.49
P(2,3D)-14k	293	0.1	4	24%	15.6	13.6	18.9	1.40
P(2,4D)-17k	104	0.1	2.5	60%	13.9	17.3	21.3	1.23
P(2,4D)-23k	204	0.1	4	60%	27.7	23.2	31.1	1.34
P(2,4D)-30k	151	0.1	6	89%	30.0	30.2	38.9	1.29
P(2,6D)-24k	219	0.15	3.3	53%	28.9	24.0	41.8	1.74
P(2,6D)-21k	137	0.15	6.5	87%	25.3	21.0	31.7	1.51
P(2,6D)-11k	83	0.15	5	50%	10.6	11.0	17.8	1.62
P(2,6D-*co*-3,5D)-21k	134	0.1	5	84%	25.1	21.3	26.8	1.26
P(2,6D-*co*-2,4D)-20k	138	0.1	5	88%	27.0	20.2	26.1	1.29

[a]The number following the polymer name denotes the molecular weight (g/mol) [k denotes thousands] as determined by SEC. [b]Initial molar ratio of monomer to CTA. [c]Initial molar ratio of AIBN to CTA. [d]Monomer conversion, determined *via* ^{1}H NMR spectroscopy. [e]Calculated molecular weight on the basis of monomer conversion. [f]Determined from SEC tests (described in **Materials and Experimental Methods** section).

Table S2: T_g's of homopolymers and statistical copolymers, along with $T_{g,\infty}$ values calculated using the Flory-Fox equation

Polymer	M_n (kg/mol)	T_g (°C)	$T_{g,\infty}$ (°C)
P(3,5D)	38	93.5	110
	33	90.3	
	23	81.5	
P(2,3D)	20	108.1	120
	16	105.2	
	14	102.6	
P(2,4D)	30	115.1	120
	23	111.2	
	17	110.3	
P(2,6D)	24	205.2	222
	21	203.4	
	11	185.6	
P(2,6D-*co*-3,5D)[a]	21	158.1	--
P(2,6D-*co*-2,4D)[b]	20	154.0	--

[a]Polymer composition (mol/mol): $F_{2,6D} = 0.64$, $F_{3,5D} = 0.36$. [b]Polymer composition (mol/mol): $F_{2,6D} = 0.41$, $F_{2,4D} = 0.59$.

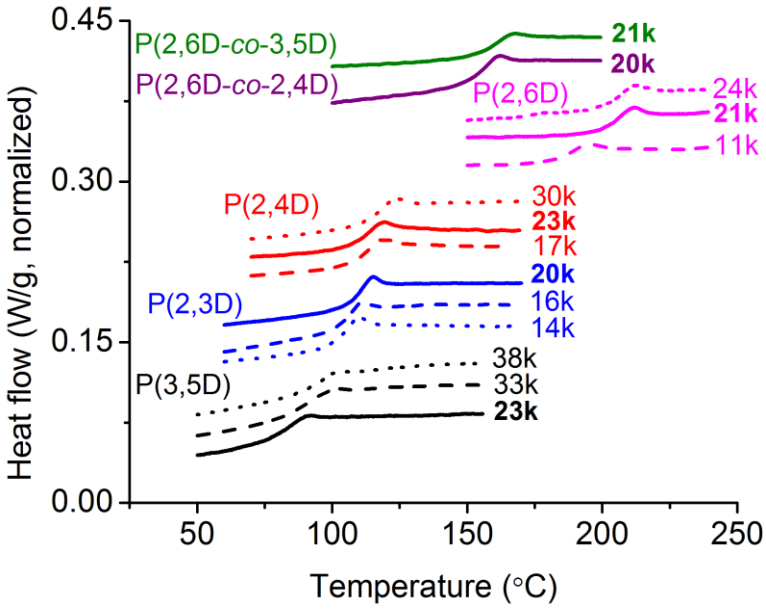

Figure S1. DSC thermograms (endotherm up) for all homopolymers and statistical copolymers. Data were normalized to the slope above T_g and shifted vertically for clarity.

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