

Supporting Information (SI)

Syringyl Methacrylate, a Hardwood Lignin-Based Monomer for High- T_g Polymeric Materials

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Materials and Methods

Synthesis and characterization of syringyl methacrylate (SM, 2,6-dimethoxyphenyl methacrylate).

SM was synthesized and purified using a procedure adapted from guaiacylic methacrylate synthesis methods.¹ Syringol (99%, Fisher Scientific, used as received) was acylated with 1.02 molar equivalents of methacrylic anhydride (94%, inhibited with 2000 ppm Topanol A, Sigma-Aldrich, used as received) using catalytic amounts of 4-dimethylaminopyridine (DMAP, >99%, Sigma-Aldrich, recrystallized from toluene), a reaction temperature of 60 °C, and reaction times between 24 h and 72 h. Syringol-to-SM conversions of >60 mol-% were achieved at higher DMAP contents (*i.e.*, 0.06 mol/mol DMAP/methacrylic anhydride instead of 0.02 mol/mol DMAP/methacrylic anhydride in reference 1). After washing SM in dichloromethane with a saturated sodium bicarbonate solution, 1.0 M NaOH, 0.5 M NaOH, 1.0 M HCl, and deionized water in accordance with reference 1 and then concentrating the product by rotary evaporation, SM was fractionated to high purity using a heat–decant–cool cycle in either hexanes or petroleum ether. The monomer/hydrocarbon mixture was heated to reflux while stirring and subsequently decanted into a new flask, partially separating the SM from insoluble viscous orange byproducts. Upon cooling, SM phase-separated from the supernatant. This procedure was repeated with the SM/hexanes (or petroleum ether) mixture until the phase-separating SM layer vitrified at room temperature, at which point the product was collected by Buchner filtration (7 wt-% yield, >98 mol-% purity or >99 mol-% if recrystallized once more from ethanol). Alternatively, the washed and concentrated SM was purified by automated column chromatography (Silica gel, stepped elution of 1:9 [3 column volumes] to 2:8 [8 column volumes] v/v ethyl acetate in hexanes, >98 mol-% purity) and then recrystallized once from ethanol (>99 mol-% purity). ¹H NMR δ ppm (CDCl₃, 600 MHz): 7.14 (1H, dd, *J* = 12 Hz, 12 Hz), 6.63 (2H, d, *J* = 12 Hz), 6.40 (1H, q, *J* = 1.2 Hz), 5.76 (1H, q, *J* = 1.5 Hz), 3.82 (6H, s), 2.09 (3H, dd, *J* = 1.2 Hz, 1.4 Hz).

Synthesis and characterization of PSM and heteropolymers.

Polymers were synthesized and purified following procedures previously reported for softwood lignin-based methacrylate homopolymers and heteropolymers.^{2, 3} The components of the heteropolymers included one or more of the following in addition to SM: 4-ethylguaiacyl methacrylate (EM, 4-ethyl-2-methoxyphenyl methacrylate), vanillin methacrylate (VM, 4-formyl-2-methoxyphenyl methacrylate), and/or creosyl methacrylate (CM, 4-methyl-2-methoxyphenyl methacrylate). Two heteropolymer compositions approximately mimicked fractionated Organosolv switchgrass lignin-based bio-oils based on the relative contents of guaiacol derivatives and syringol derivatives.⁴

Reaction conditions and size-exclusion chromatography (SEC) data for the homopolymers and heteropolymers are reported in Table S1. Note: macromolecular characterization equipment details are provided as footnotes to the table. Monomer compositions, monomer-to-polymer conversions (x), and cumulative polymer compositions were determined using a method described in literature,³ the vinyl peaks for SM listed above (6.40 ppm and 5.76 ppm), and the polymer peaks (fit using MestReNova Software⁵) indicated below. Spectra were analyzed in triplicate to determine the 95% confidence in the composition, conversion, and tacticity measurements.

Poly(syringyl methacrylate) [PSM]: ¹H NMR δ ppm (CDCl₃, 600 MHz): 7.18–6.79 (1H, br), 6.67–6.14 (2H, br), 3.94–3.30 (6H, br), 3.30–1.35 (5H, many br). Non-ambient temperature (58 °C) ¹H NMR data (CDCl₃ with 5 wt-% trifluoroacetic anhydride, 400 MHz) were utilized for tacticity estimates. The α -methyl protons (1.90–1.45 ppm) were split into broad peaks representative of triads with approximate chemical shifts of 1.76 ppm (*mm*), 1.69 (*mr* and *rm*), and 1.64 ppm (*rr*), which were used to estimate tacticity. These triad peaks were assumed to be located in the same order as the analogous triad protons in poly(methyl methacrylate) and poly(phenyl methacrylate),^{6,7} in which *mm* is further downfield and *rr* is further upfield relative to the single *mr/rm* peak. The fractions of racemo diads (f_r) of 0.90 ± 0.05 and syndiotactic triads (f_{rr}) of 0.85 ± 0.09 for PSM-21 are greater than the f_r of ~ 0.75 (and f_{rr} of ~ 0.60) reported for the softwood polymers,⁸ which are considered atactic.

Poly(4-ethylguaiacyl methacrylate-*co*-syringyl methacrylate) [P(ES)]: ¹H NMR δ ppm (CDCl₃, 600 MHz): 7.15–6.79 (1H/EM + 1H/SM, br), 6.79–6.24 (2H/EM + 2H/SM, 3 br), 3.94–3.30 (3H/EM + 6H/SM, br), 3.30–1.24 (5H/EM + 5H/SM, many br), 1.24–1.00 (3H/EM, br). Polymer composition was determined *via* the characteristic EM peak at 1.24–1.00 ppm. The area of the peak was referenced to the area of the aromatic proton peaks (7.15–6.79 ppm and 6.79–6.24 ppm) and the methoxy proton peak (3.94–3.30 ppm) to estimate error. Monomer feed composition (mol/mol): $f_{EM}=0.951 \pm 0.003$, $f_{SM} = 0.049 \pm 0.003$. Polymer composition (mol/mol): $F_{EM}=0.95 \pm 0.02$, $F_{SM} = 0.05 \pm 0.02$.

Poly(creosyl methacrylate-*co*-4-ethylguaiacyl methacrylate-*co*-syringyl methacrylate) [P(CES)]: ¹H NMR δ ppm (CDCl₃, 600 MHz): 7.15–6.81 (1H/CM + 1H/EM + 1H/SM, br), 6.81–6.52 (2H/CM + 2H/EM, 2 br), 6.52–6.30 (2H/SM, br), 3.87–3.30 (3H/CM + 3H/EM + 6H/SM, br), 3.30–1.27 (5H/CM + 5H/EM + 5H/SM, many br), 1.24–1.00 (3H/EM, br). Polymer composition was determined using the characteristic EM peak at 1.24–1.00 ppm and the characteristic SM peak at 6.52–6.30 ppm. The areas of these peaks were referenced to the area of the aromatic proton peaks

(7.15–6.81 ppm and 6.81–6.30 ppm) and the methoxy proton peak (3.87–3.30 ppm) to estimate error. Monomer feed composition (mol/mol): $f_{CM} = 0.191 \pm 0.003$, $f_{EM} = 0.339 \pm 0.004$, $f_{SM} = 0.469 \pm 0.004$. Polymer composition (mol/mol): $F_{CM} = 0.16 \pm 0.03$, $F_{EM} = 0.36 \pm 0.03$, $F_{SM} = 0.48 \pm 0.02$.

Poly(vanillin methacrylate-*co*-4-ethylguaiacyl methacrylate-*co*-syringyl methacrylate) [P(VES)]: ^1H NMR δ ppm (CDCl_3 , 600 MHz): 9.94–9.44 (1H/VM, br), 7.45–7.18 (3H/VM, br), 7.18–6.79 (1H/EM + 1H/SM, br), 6.75–6.30 (2H/EM + 2H/SM, 2 br), 3.82–3.30 (3H/VM + 3H/EM + 6H/SM, br), 3.30–1.24 (5H/VM + 5H/EM + 5H/SM, many br), 1.24–1.00 (3H/EM, br). Polymer composition was determined using the characteristic EM peak at 1.24–1.00 ppm and the characteristic VM peaks at 9.94–9.44 ppm and 7.45–7.18 ppm. The areas of these peaks were referenced to the area of the aromatic proton peaks (7.48–6.30 ppm) and the methoxy proton peak (3.82–3.30 ppm) to estimate error. Monomer feed composition (mol/mol): $f_{VM} = 0.226 \pm 0.007$, $f_{EM} = 0.227 \pm 0.003$, $f_{SM} = 0.548 \pm 0.007$. Polymer composition (mol/mol): $F_{VM} = 0.24 \pm 0.02$, $F_{EM} = 0.23 \pm 0.01$, $F_{SM} = 0.53 \pm 0.02$.

Table S1. Polymerization conditions^a and characteristics of polymers containing SM segments

	$[\text{M}]_0/[\text{C}]_0^b$ (mol/mol)	$[\text{M}]_0/[\text{S}]^b$ (wt/wt)	t (h)	x (mol/mol)	$M_{n,\text{calc}}^c$ (kDa)	$M_{n,\text{RI}}^d$ (kDa)	$M_{n,\text{LS}}, M_{w,\text{LS}}^e$ (kDa)	$D^{\text{d,f}}$	T_g (°C)
PSM-24	219	0.94	3.3 ^g	0.53	29	24	-	1.74	205
PSM-21	137	0.94	6.5	0.87	25	21	-	1.51	203
PSM-11	83	0.50	5.0	0.50	11	11	-	1.62	185
PSM-A ^{h,i}	285	0.96	0.3 ^g	0.53	37	38	-	1.61	-
PSM-B ^h	229	0.53	1.5	0.33	22	20	-	1.73	-
PSM-C	120	0.92 ^j	2.8	0.56	16	17	-	1.61	-
PSM-D	131	0.52 ^j	9.0	0.86	23	21	-	1.47	-
P(VES)	229	0.94	5.5	0.82	39	36	35, 52	1.45 (1.50 ^e)	159
P(CES)	231	0.94	5.5	0.78	37	32	35, 47	1.38 (1.32 ^e)	154
P(ES)	231	0.94	5.5	0.76	36	33	36, 46	1.32 (1.30 ^e)	114

^aThe homopolymers labeled by numbers and heteropolymers were synthesized at 72 °C in anisole with 5 wt-% *N,N*-dimethylformamide as an internal standard and with an initiator (I, 2,2'-azobisisobutyronitrile [AIBN]) to chain-transfer agent (C, 2-cyano-2-propylbenzodithioate) ratio of 0.155 ± 0.005 mol/mol. Polymers labeled by letters deviated from this procedure as indicated *via* superscripts h, i, and j. ^bAbbreviations stand for monomer (M) and solvent (S). ^cSee below for equation. ^dDetermined relative to polystyrene standards using data from SEC with refractive-index (RI) detectors and a chloroform eluent. ^eDetermined by Zimm analysis using data from SEC with a tetrahydrofuran (THF) eluent and light-scattering (LS) detectors. ^fFor comparison, a PSM prepared by free-radical polymerization had a D of 2.65, and PSMs prepared with an ineffective chain-transfer agent had D 's of 2.14 and 2.39. ^gReaction vitrified. ^hReaction temperature was 90 °C. ⁱ $[\text{I}]_0/[\text{C}]_0 = 0.32 \pm 0.05$ mol/mol. ^jSolvent was chlorobenzene.

The values for $M_{n,\text{calc}}$ in Table S1 were determined using the following equation:^{2,9,10}

$$M_{n,\text{calc}} = \frac{[M]_0 \cdot x \cdot M_{\text{monomer}}}{[C]_0 \cdot (1 - (1 - x)^{C_{\text{tr,app}}}) + d \cdot f \cdot [I]_0 \cdot (1 - e^{-k_d \cdot t})} + M_C \quad (\text{S1})$$

M_{monomer} (compositional average of the monomer molecular weights) =

222 g/mol for PSM syntheses

221 g/mol for P(VES) synthesis

219 g/mol for P(CES) synthesis

220 g/mol for P(ES) synthesis

M_C (molecular weight of C) = 221 g/mol

f (initiation efficiency of I) = 0.5⁹

k_d (decomposition rate of I) $\approx 5.7 \times 10^{-5} \text{ s}^{-1}$ at 72 °C or $5.4 \times 10^{-4} \text{ s}^{-1}$ at 90 °C¹¹

d (number of chains produced in a methyl methacrylate-like radical–radical termination event) = 1.67⁹

$C_{\text{tr,app}}$ (apparent chain-transfer coefficient) ≈ 2.6 for hardwood and softwood monomers polymerized under the given reaction conditions (based on data in this manuscript and elsewhere³). $C_{\text{tr,app}}$ also was assumed to be ≈ 2.6 for reactions performed under different conditions (the PSMs labeled by letters, which either had S = chlorobenzene or a reaction temperature of 90 °C), noting that this factor affects $M_{n,\text{calc}}$ by <1% for PSM-C and PSM-D but could cause $M_{n,\text{calc}}$ to be overestimated by up to 14% for PSM-A, 34% for PSM-B, and 11% for PSM-C.

Equation S1 accounts for chains initiated by free radicals and the approximate time-dependent consumption of chain-transfer agent. The corresponding equation for the maximum number-average degree of polymerization ($X_{n,\text{max}}$ from the manuscript) assumes 100% consumption of the chain-transfer agent at all conversions, no chains initiated by free radicals, and no contribution of M_C .

Equipment

^1H NMR data were collected and analyzed following a previously reported methodology.^{3,8} SEC data for the PSM homopolymers and heteropolymers (relative to polystyrene standards) were determined on an Agilent HP 1100 instrument with chloroform as the eluent (1.0 mL/min, HP 1047A RI Detector, Carian PLgel Mixed-C columns in series). Additional SEC data with light-scattering were determined for the heteropolymers using a Viscotek VE 3580 instrument with tetrahydrofuran (THF) as the eluent (1.0 mL/min; Viscotek VE3580 RI, UV-PDA, and Viscotek 270 Dual detectors; Waters Styragel HR1 and HR4 columns [7.8 × 300 mm] in series). Analogous light-scattering SEC experiments were not performed on the PSM homopolymers due to their poor solubility in THF.

Thermogravimetric analysis (TGA, 10 °C/min under airflow), differential scanning calorimetry (DSC, 5 °C/min under air), and dynamic mechanical analysis (DMA) data were collected and analyzed as described in the literature to facilitate comparisons to softwood lignin-based polymers,⁸ but with minor differences indicated as follows. Temperature windows for DSC analysis [40–180 °C for PEM; 60–180 °C for P(ES); 60–190 °C for P(CES) and P(VES); and 140–240 °C for PSM] were chosen to minimize end-group thermolysis while also generating an above- T_g baseline of at least 20 °C to facilitate analysis. Samples for DMA (0.3 mm in thickness, 8 mm in diameter) were prepared by pressing polymer powder at high temperature [150 °C for P(ES); 190 °C for P(CES) and P(VES); and 240 °C for PSM-21] and pressure (1 metric ton) for 15 min. Frequency sweeps were taken at 10 °C temperature intervals, beginning near the T_g and ending either when the polymer flowed out from between the parallel plates or slightly below the thermal degradation onset. Temperature sweeps were taken at 3 °C/min at a frequency of 6.28 rad/s. Strain amplitudes [frequency sweep: 0.1–5% for P(ES), 0.06–5% for P(CES), 0.1–5% for P(VES), and 0.2–1% for PSM-21; temperature sweep: 0.05–5% for P(ES), 0.04–5% for P(CES), 0.06–5% for P(VES), and 0.1–1.5% for PSM-21] were varied to keep within the linear regime. Data were shifted to a reference temperature of 180 °C (the maximum temperature before polymer flow) for P(ES) and 220 °C (the only overlapping temperature) for all other macromolecules using time–temperature superposition.

Table S2. Selected characteristics of SM-containing heteropolymers to facilitate comparison^a

	P(ES)	P(CES)	P(VES)
$k_{p,app}^b$ (h ⁻¹)	0.23 ± 0.01	0.26 ± 0.02	0.26 ± 0.02
$C_{tr,app}^c$	3.0 ± 0.3	2.5 ± 0.3	2.3 ± 0.7
$T_{g,calc}^d$ (°C)	114 ± 3	153 ± 3	162 ± 3
$T_{g,meas}^e$ (°C)	114 ± 1	154 ± 1	159 ± 1
T_o^f (°C)	256 ± 5	264 ± 5	260 ± 5
η_0^g (kPa·s)	0.2 ^h	37	39

^aValues reported with 95% confidence intervals if available. ^bApparent propagation rate normalized to an initiator-to-chain-transfer ratio of 0.100. ^cApparent chain-transfer coefficient determined using the Mayo equation and the change in dispersity at low conversions. ^d T_g calculated using the Fox equation and T_g 's of similar molecular weight homopolymers (130 °C for PVM, 110 °C for PEM, 126 °C for PCM, and 205 °C for PSM).⁸ ^eAverage T_g from the midpoint of the inflection in the second and third heat of the DSC data (5 °C/min). ^fOnset degradation temperature determined in air using TGA (10 °C/min). ^gZero-shear viscosity at 220 °C determined by the Cox–Merz rule. ^hValue extrapolated from data collected at 160–180 °C assuming Arrhenius behavior.

Supporting Figures

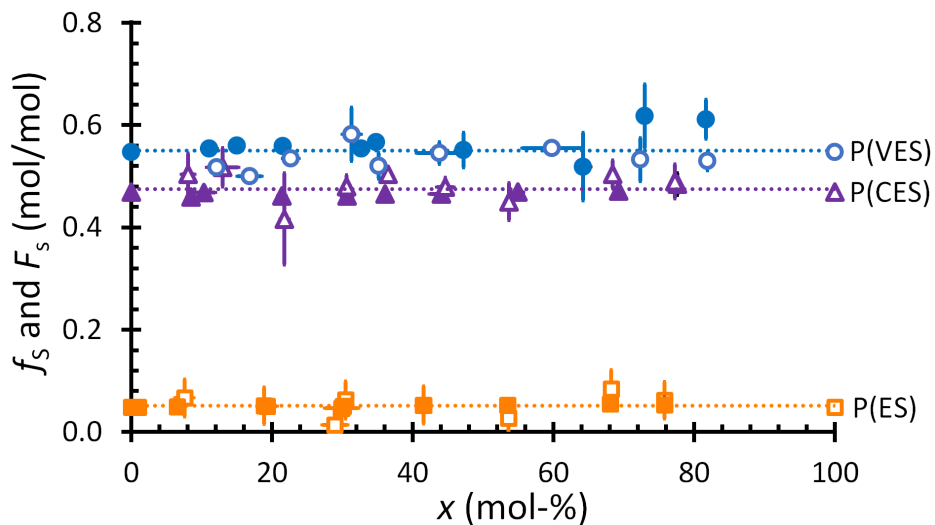


Figure S1. Fraction of SM monomer relative to the other monomers in the reaction mixture (f_s , closed symbols) and cumulative fraction of SM segments in the polymer chains (F_s , open symbols) vs. monomer-to-polymer conversion (x), as determined from ^1H NMR data of polymerization aliquots. Horizontal lines correspond to the average composition based on all of the data points for a given heteropolymer. The insignificant change in composition indicates that the reactivity ratios between hardwood and softwood methacrylate monomers are nearly unity (*i.e.*, these heteropolymers have an approximately random distribution of monomer segments).

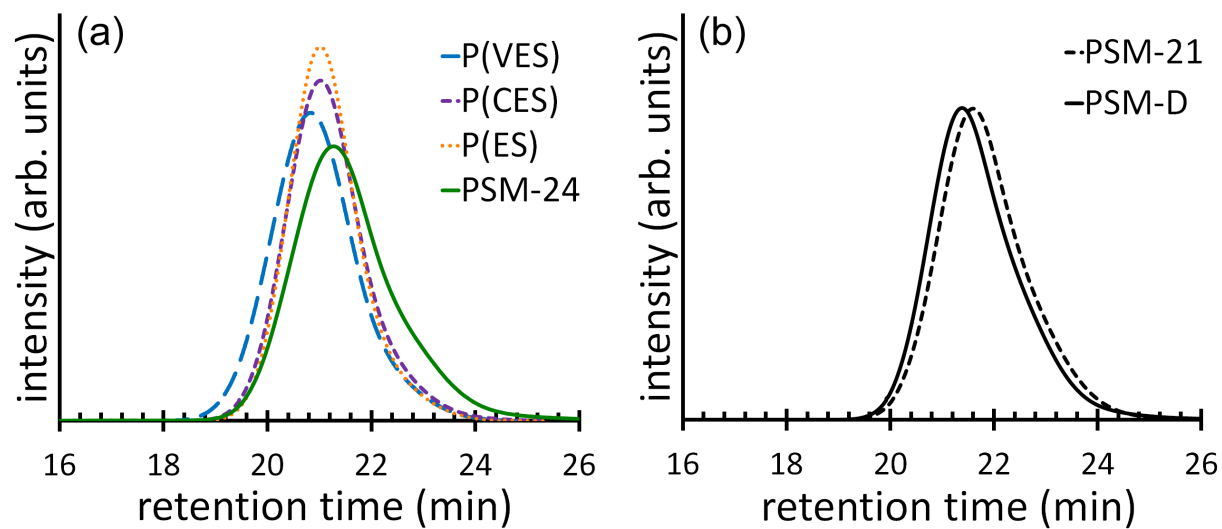


Figure S2. SEC data collected in chloroform for (a) the polymers chosen for DMA analysis and (b) selected PSMs prepared using the various conditions listed in Table S1. These data all indicate unimodal molecular weight distributions.

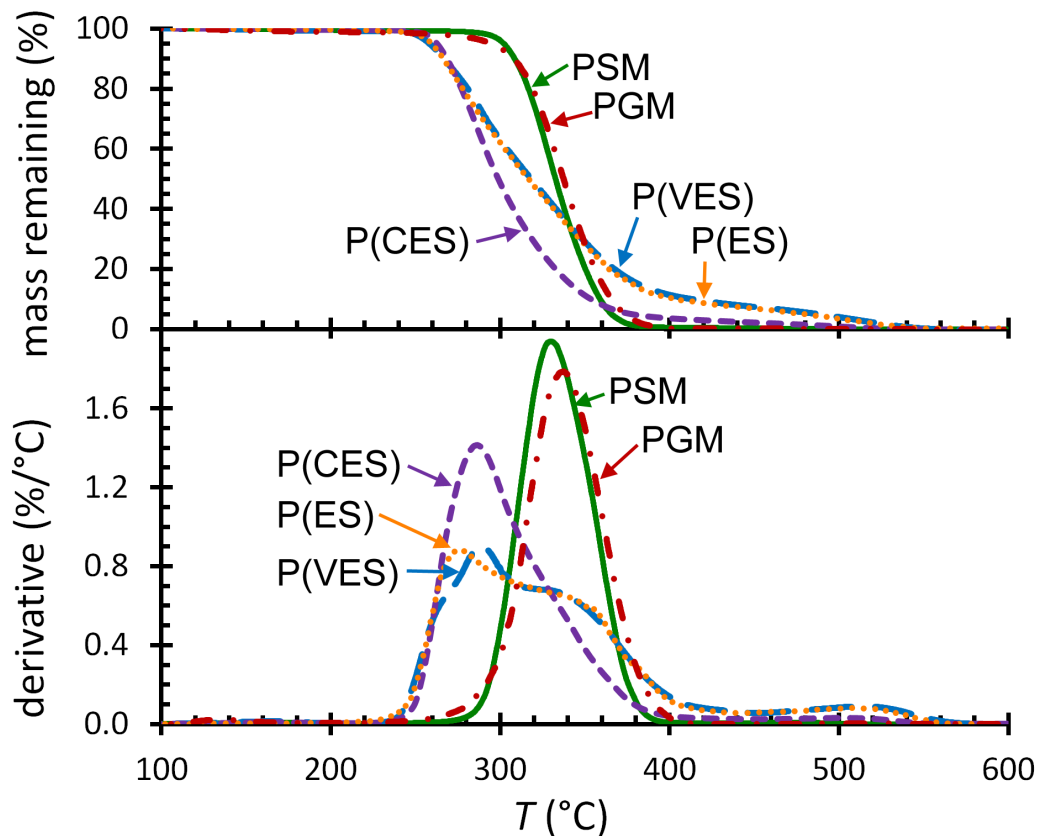


Figure S3. (top) Mass loss vs. temperature data and (bottom) the corresponding mass loss derivative vs. temperature data for example homopolymers, PSM-21 and poly(guaiacyl methacrylate) [PGM, poly(2-methoxyphenyl methacrylate)], and heteropolymers, as determined by TGA (10 °C/min under airflow). The onset of degradation is the same for all of the heteropolymers, as it depends on the least stable (EM) segments.⁸

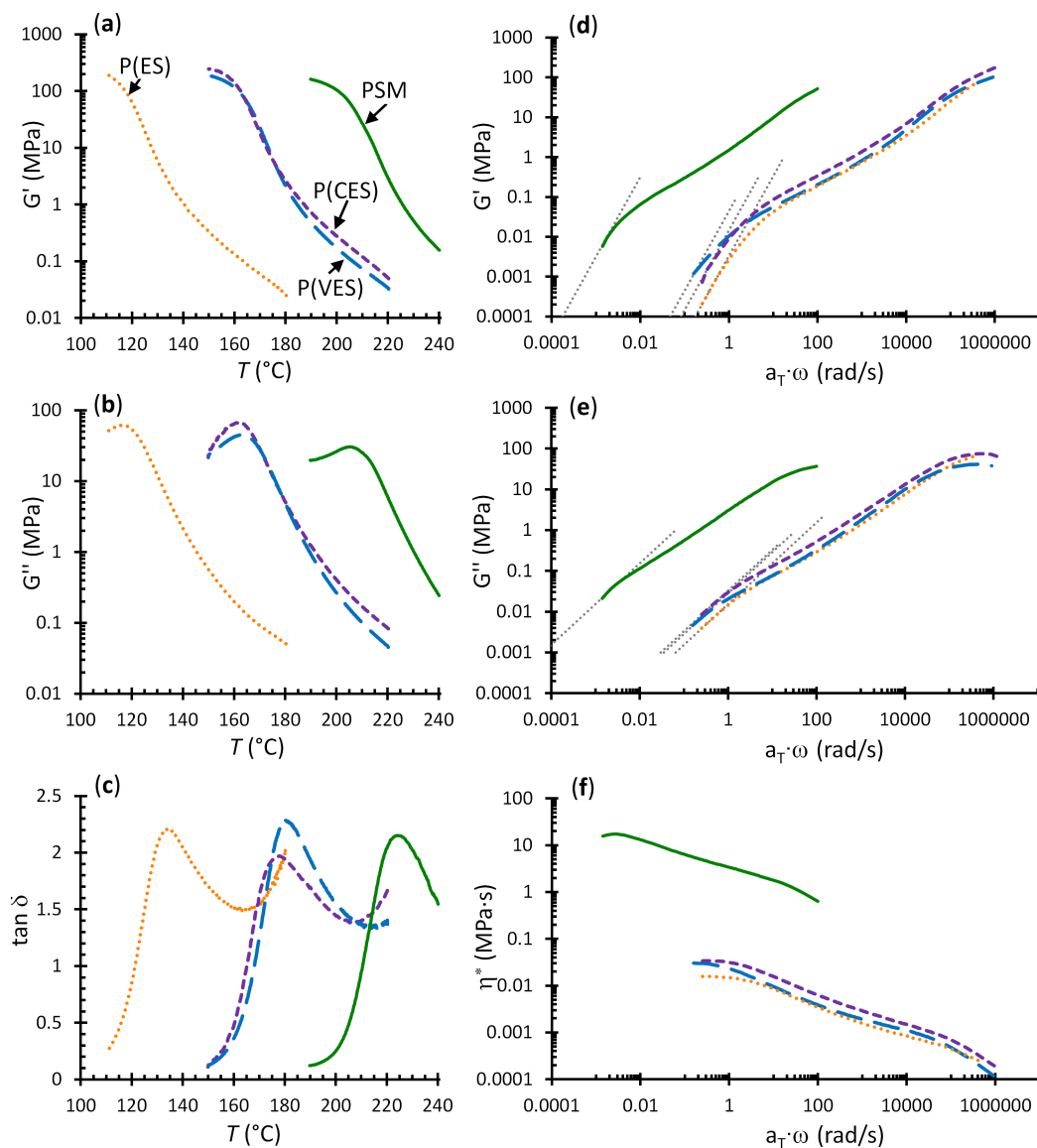


Figure S4. DMA data for PSM-21 and SM-containing heteropolymers, in which G' is the elastic shear modulus, G'' is the loss shear modulus, $\tan \delta$ is the dissipation factor, η^* is the complex viscosity, T is the temperature, a_T is the shift factor [see also Fig. 3a, in which $\eta_0 = a_T \cdot \eta_0(T_{\text{ref}})$], and ω is the frequency. The labels on the lines in panel (a) correspond to all panels. Panels (a), (b), and (c) were taken at a constant ω of 6.28 rad/s. Panels (d), (e), and (f) were prepared utilizing time–temperature superposition and a reference temperature of 220 °C for all but P(ES), which has a reference temperature of 180 °C (the maximum temperature before the polymer flowed out from between the instrument plates). The dotted gray lines in (d) and (e) have slopes of two and one, respectively, illustrating the expected slope for polymers with minimal intermolecular interactions in the melt state. Panels (a)–(e) indicate that the rheological properties, and their changes with respect to T or ω , are similar for all polymers, except for the shift to lower T 's or ω 's at higher SM contents, and panel (f) highlights the disparate viscosity of PSM in comparison to P(CES) and P(VES) at the same reference temperature, while also showing the similar behavior of P(ES), P(CES), and P(VES) when shifted to differing reference temperatures (180 °C or 220 °C).

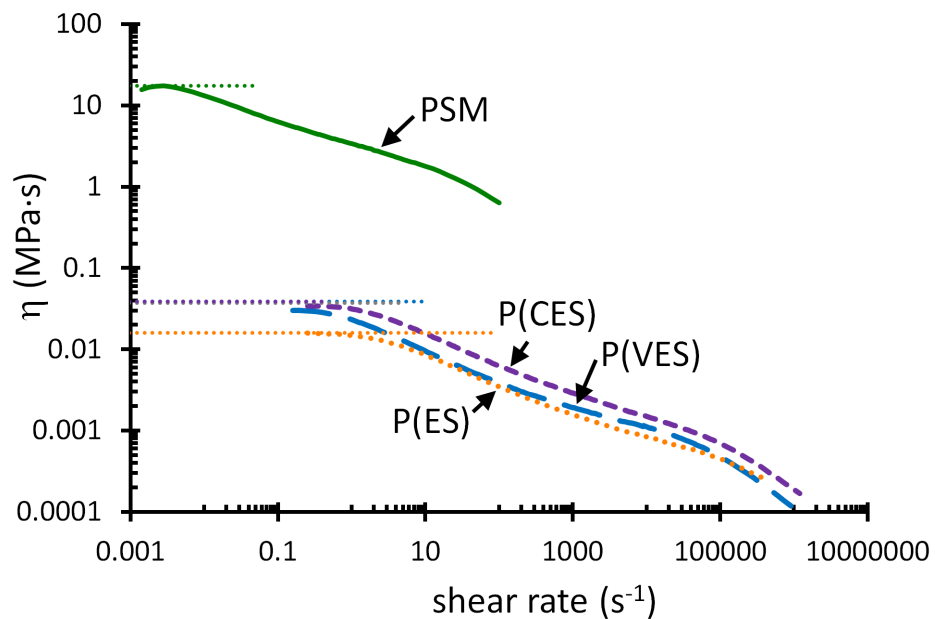


Figure S5. Steady shear viscosities determined *via* the data from Figure S4 and the Cox–Merz rule, $\eta^*(\omega)|_{\omega=\dot{\gamma}} = \eta(\dot{\gamma})$, in which $\dot{\gamma}$ is the shear rate, and η is the dynamic viscosity. Extrapolation of the data to the Newtonian plateau gave the zero-shear viscosities, η_0 , at the reference temperature [220 °C for all but P(ES), which has a reference temperature of 180 °C]. These $\eta_0(T_{\text{ref}})$'s are represented by horizontal dotted lines and were used to generate the η_0 vs. T data in the manuscript [Fig. 3a; $\eta_0 = a_T \cdot \eta_0(T_{\text{ref}})$].

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