

Supporting Information

Increased hydrophilicity of lignin-derivable vs. bisphenol-based polysulfones for water filtration applications

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1. Materials and reagents:

Bisphenol A (BPA, $\geq 99\%$), guaiacol ($\geq 98\%$, food grade), vanillyl alcohol ($\geq 98\%$), thioglycolic acid (98%), Amberlyst® 15 hydrogen form (dry), 4,4'-difluorodiphenyl sulfone (DFDPS, 99%), diatomaceous earth (Celite® 545), diiodomethane (99%), and potassium carbonate (K_2CO_3 , $\geq 99\%$) were purchased from Sigma-Aldrich. Bisphenol F (BPF, $> 99.0\%$) was purchased from TCI Chemicals. *N,N*-Dimethylacetamide (DMAc, 99.0%) and deuterated chloroform ($CDCl_3$, 99.8 atom% D, with 0.03% v/v TMS) were acquired from Acros Organics. Chloroform ($\geq 95\%$) was procured from Macron Fine Chemicals. Toluene (99.8%), tetrahydrofuran (THF Optima™, $\geq 99.9\%$), HCl (36.5 - 38%), magnesium sulfate (anhydrous), acetone (99%), hexanes (99%), ethyl acetate ($\geq 99.5\%$), acetonitrile ($\geq 99.9\%$), sodium bicarbonate ($\geq 99.7\%$), dichloromethane (DCM, $\geq 99.9\%$), and NaCl ($\geq 99.5\%$) were purchased from Fisher Scientific. *N,N*-Dimethylformamide (DMF, $\geq 99.8\%$) and methanol ($\geq 99.8\%$) were sourced from VWR Chemicals BDH®. N_2 (ultra-high purity [UHP], 99.999%) was obtained from Airgas Inc., facilitated by Arizona State University gas services. Ar (grade 5) was purchased from Keen Compressed Gas. BPA, BPF, and DFDPS were placed in an oven at 60 °C for 48 h, K_2CO_3 was stored in an oven at 130 °C, and acetone was passed through a magnesium sulfate column before use. Toluene and THF Optima™ were purified using an MBraun SPS-800 solvent purification system prior to use. All other chemicals were used as received.

2. Synthesis

2.1 Monomer (lignin-derivable bisguaiacols) synthesis

2.1.1 Bisguaiacol A (BGA) synthesis: BGA was synthesized by the acid-catalyzed condensation of guaiacol and acetone.¹⁻³ For BGA synthesis, guaiacol (40 g, 0.32 mol) and acetone (3.4 mL, 0.046 mol) were loaded in an oven-dried, single-neck, round-bottom flask (250 mL) equipped with a condenser and magnetic stirrer. Then, 5 mL of concentrated HCl (6 g, 15 wt% relative to guaiacol) and thioglycolic acid (0.2 vol% with respect to the catalyst) were slowly added to the above reactants. Acetone can undergo self-condensation to form mesityl oxide in stronger acidic conditions.⁴ This mesityl oxide can further react with guaiacol. Thus, the BGA synthesis was conducted in an excess of guaiacol and in the presence of an acid promoter (thioglycolic acid) to minimize by-product formation from the self-condensation of acetone.⁴ The reaction mixture was sparged with Ar gas (10 min) and heated to 100 °C in a silicone oil bath for 24 h. After 24 h, the reaction mixture was passively cooled to ~20 °C in the air for 1.5 h, and the crude mixture was dissolved in DCM (15 mL). The organic phase was washed with sodium bicarbonate until the aqueous layer reached neutral pH, then washed with deionized (DI) water (3 times) and a brine solution (2 times). The organic phase was collected, the solvent was removed under reduced pressure, and the product was purified by flash column chromatography (Biotage® Selekt Systems, Biotage® Sfär Silica columns 60 μm , 100 g) with ethyl acetate (25% v/v) and hexanes (75% v/v). The product was dried at 50 °C under vacuum for 24 h. BGA was obtained as a white solid (yield: ~40 mol%). Proton (1H) nuclear magnetic resonance (1H NMR) spectra (600 MHz, $CDCl_3$) δ 6.87 - 6.65 (m, 6H), 5.51 (d, $J = 15.9$ Hz, 2H), 3.94 - 3.76 (m, 6H),

1.65 (d, $J = 4.9$ Hz, 6H). Fourier transform mass spectrometry (FTMS) (Electrospray ionization [ESI], m/z): calcd for $C_{17}H_{20}O_4$ 288.1362; found 288.1354 (**Figure S1**).

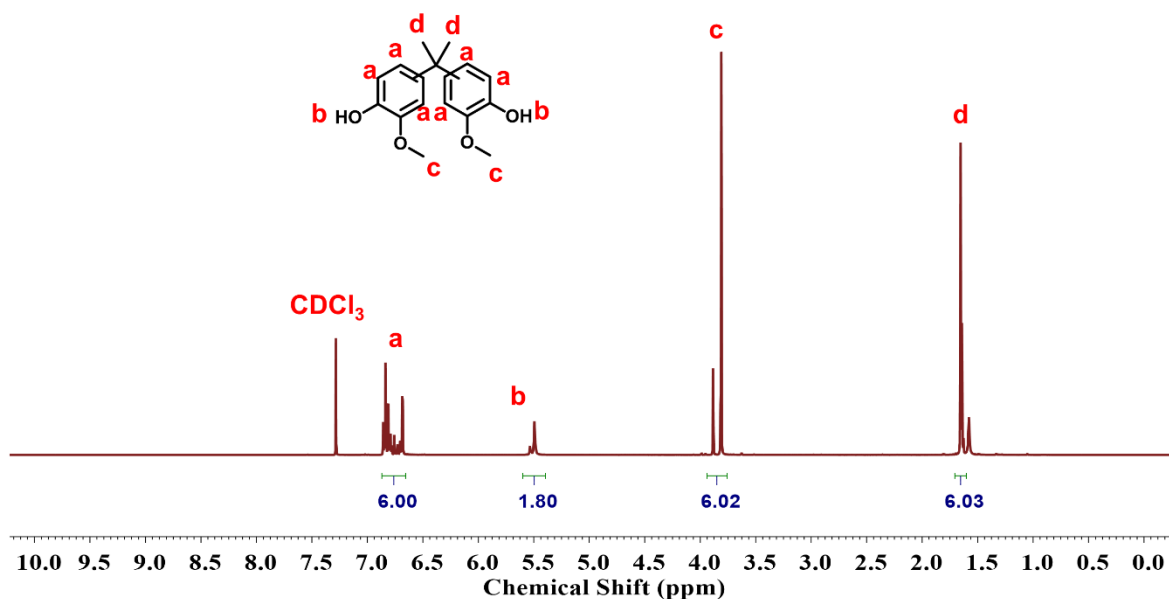


Figure S1. ^1H NMR spectrum for BGA

2.1.2 Bisguaiacol F (BGF) synthesis: BGF was synthesized as reported in the literature through an electrophilic aromatic substitution reaction between vanillyl alcohol and guaiacol.^{1, 5} Guaiacol (40 g, 0.311 mol) and vanillyl alcohol (12 g, 0.078 mol) were added into an oven-dried, single-neck, round-bottom flask (250 mL) equipped with a magnetic stir bar. The reaction mixture was heated to 70 °C in a silicone oil bath and sparged with Ar gas (40 min). Amberlyst® 15 hydrogen form (dry) [3.6 g, 30 wt% relative to the vanillyl alcohol] was then added to the reaction flask under Ar flow. The reaction was carried out at 70 °C for 18 h. After 18 h, the crude mixture was passively cooled to ~20 °C in the air for 1.5 h and dissolved in 15 mL of DCM. Amberlyst® 15 (catalyst) was separated from the crude mixture using a Buchner funnel, and the liquid phase was then transferred to a separatory funnel. The liquid phase was washed with DI water (3 times) and brine solution (2 times). The organic phase was collected, the solvent was removed under reduced pressure, and the product was purified by flash column chromatography (Biotage® Selekt Systems, Biotage® Sfär Silica columns 60 μm , 100 g) with ethyl acetate (25 v/v%) and hexanes (75 v/v%). The product was dried under vacuum at 50 °C for 24 h. BGF was obtained as a white solid (yield: ~50 mol%). ^1H NMR (600 MHz, CDCl_3) δ 6.84 - 6.51 (m, 6H), 5.41 (s, 2H), 3.76 (d, $J = 5.2$ Hz, 8H). FTMS (ESI, m/z): calcd for $C_{15}H_{16}O_4$ 260.1049; found 260.1041 (**Figure S2**).

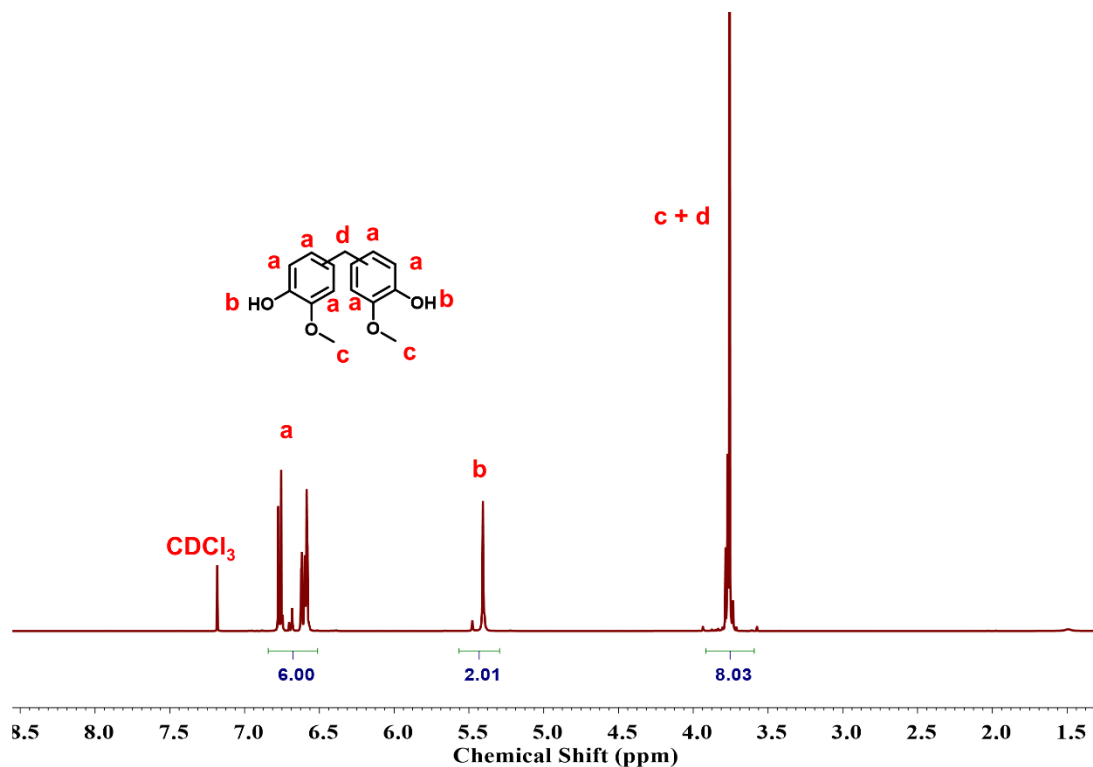


Figure S2. ¹H NMR spectrum for BGF

2.2 Polysulfones (PSfs) synthesis: PSfs were synthesized using step-growth polymerization. The synthesis of BPF-PSf is reported as a representative example.² The reaction setup consisted of a two-neck, round-bottomed flask (100 mL) equipped with a magnetic stirrer, reflux condenser, ultra-high purity (UHP) N₂ gas inlet and outlet, and a Dean-Stark trap. The following chemicals were added: BPF (3 g, 15 mmol), DFDPs (3.8 g, 15 mmol, 1 equiv.), K₂CO₃ (2.5 g, 18 mmol, 1.2 equiv.), DMAc (41.2 mL), and toluene (22.2 mL). Initially, the system was purged with UHP N₂ for 20 min and then heated to 135 °C in an oil bath. The solution was stirred at 650 rpm for 2 h under UHP N₂ at 135 °C (*i.e.*, at reflux) to remove water and toluene. After removing the residual toluene, the reaction was continued at 145 °C for 24 h under an N₂ blanket. The solution was then passively cooled to ~23 °C and diluted with chloroform (~200 mL). Subsequently, the solution was neutralized by the gradual addition of 0.1 M HCl in THF in excess, with the mixture being stirred at ~23 °C for 2 h. The mixture was then vacuum-filtered through diatomaceous earth to remove any salts. The solution was concentrated using rotary evaporation (Scilogex RE 100-pro), and the product was precipitated using methanol. The isolated BPF-PSf was dried under vacuum at 80 °C for 18 h. The PSf was redissolved in THF and reprecipitated using methanol. The final product was dried under vacuum at 160 °C for 48 h. This protocol was consistently applied across all PSfs, although the lignin-derivable PSfs were synthesized using the same molar ratios but on a smaller scale (<1.9 g). The dried polymers were obtained as white powders.

BPA-PSf: ^1H NMR (500 MHz, CDCl_3) δ 7.88 – 7.82 (m, 4H), 7.26 – 7.20 (m, 4H), 7.04 – 6.97 (m, 4H), 6.97 – 6.91 (m, 4H), 1.69 (s, 6H). (**Figure S3**)

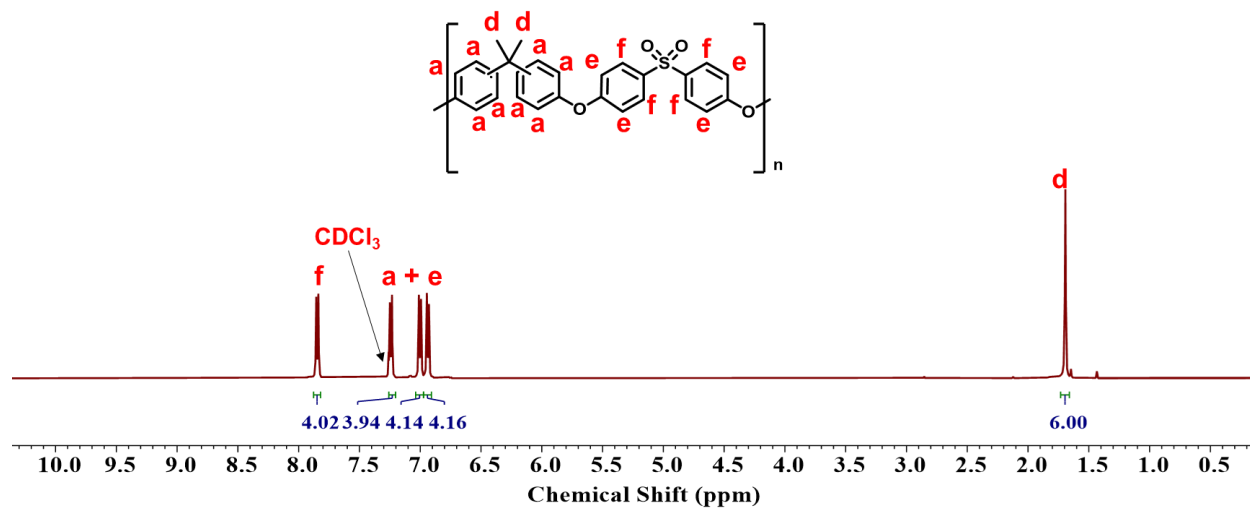


Figure S3. ^1H NMR spectrum for BPA-PSf

BPA-PSf: Carbon-13 (^{13}C) NMR (500 MHz, CDCl_3). (**Figure S4**)

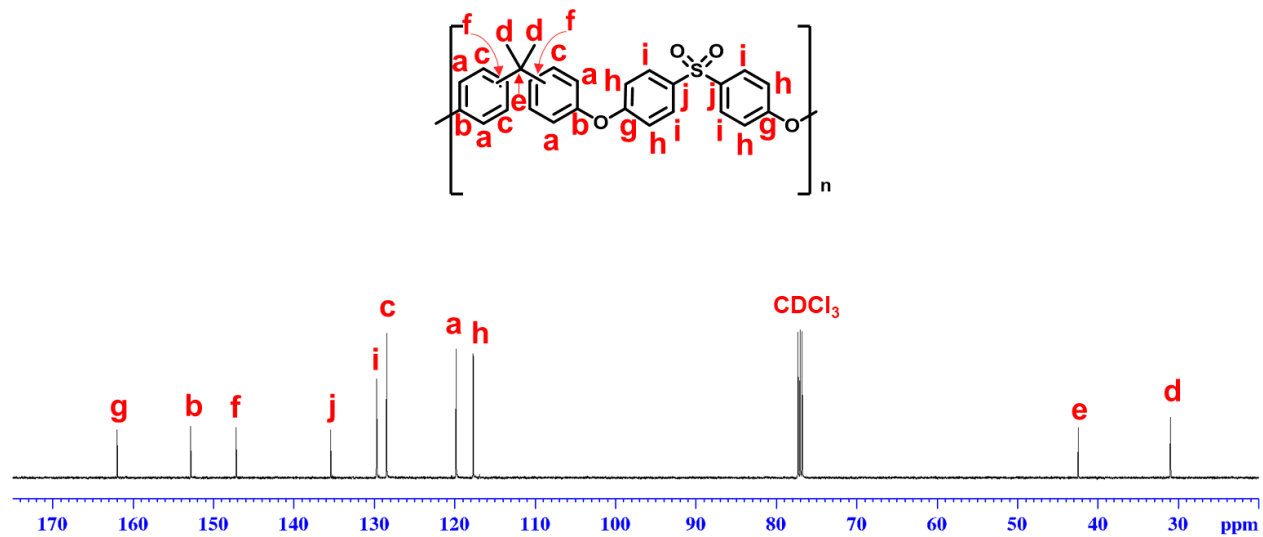


Figure S4. ^{13}C NMR spectrum for BPA-PSf

BPF-PSf: ^1H NMR (500 MHz, CDCl_3) δ 7.87 – 7.80 (m, 4H), 7.20 (d, $J = 8.2$ Hz, 4H), 7.02 – 6.92 (m, 8H), 3.98 (s, 2H). (Figure S5)

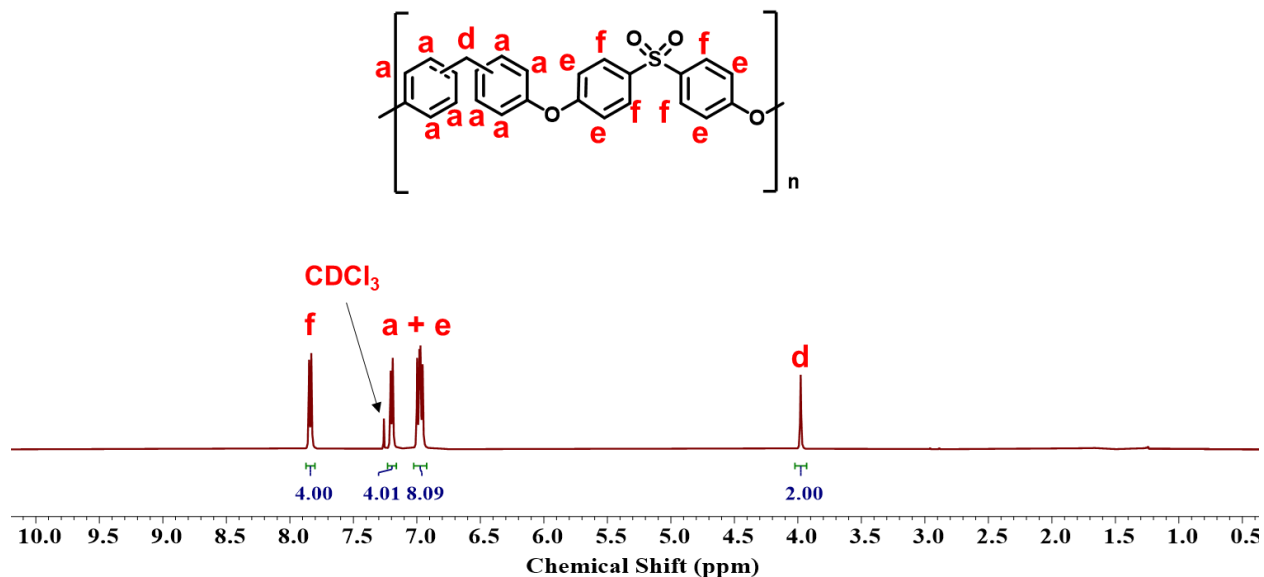


Figure S5. ^1H NMR spectrum for BPF-PSf

BPF-PSf: ^{13}C NMR (500 MHz, CDCl_3). (Figure S6)

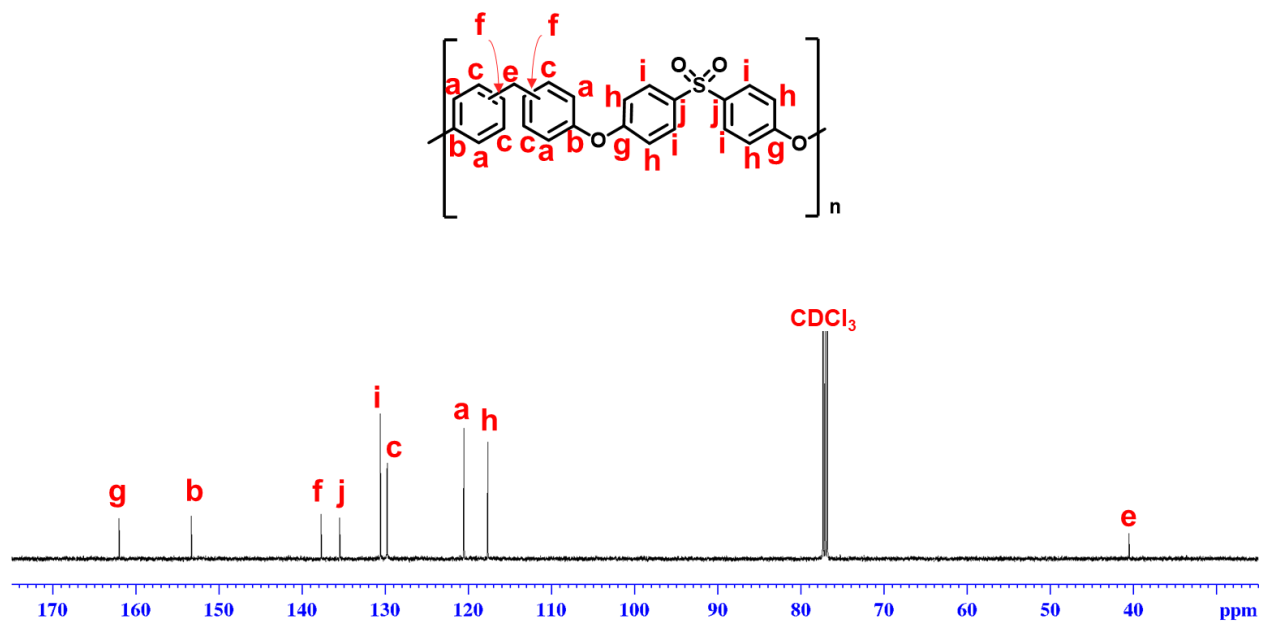
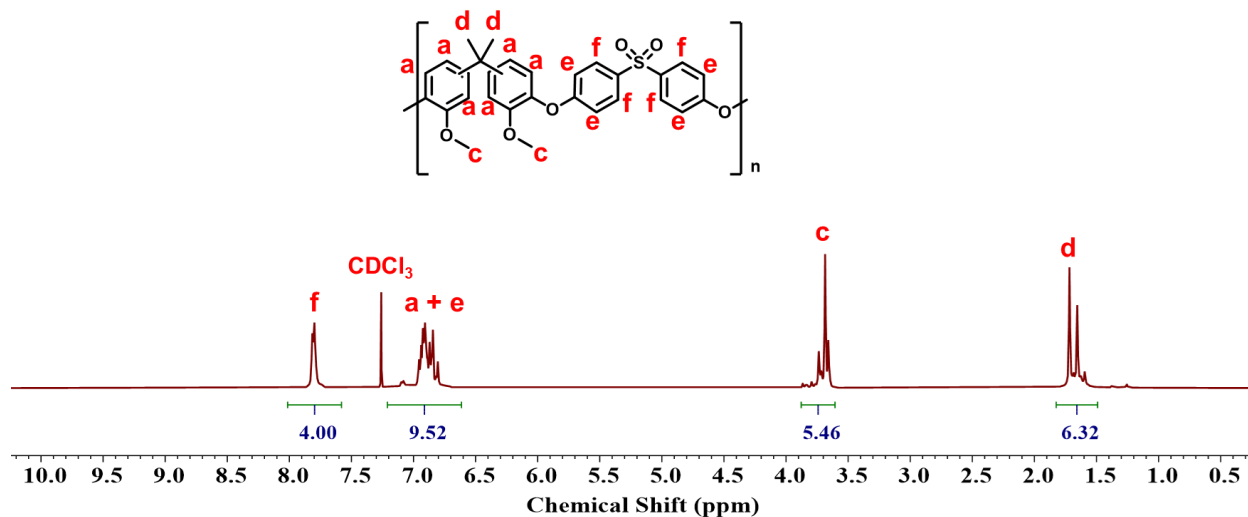
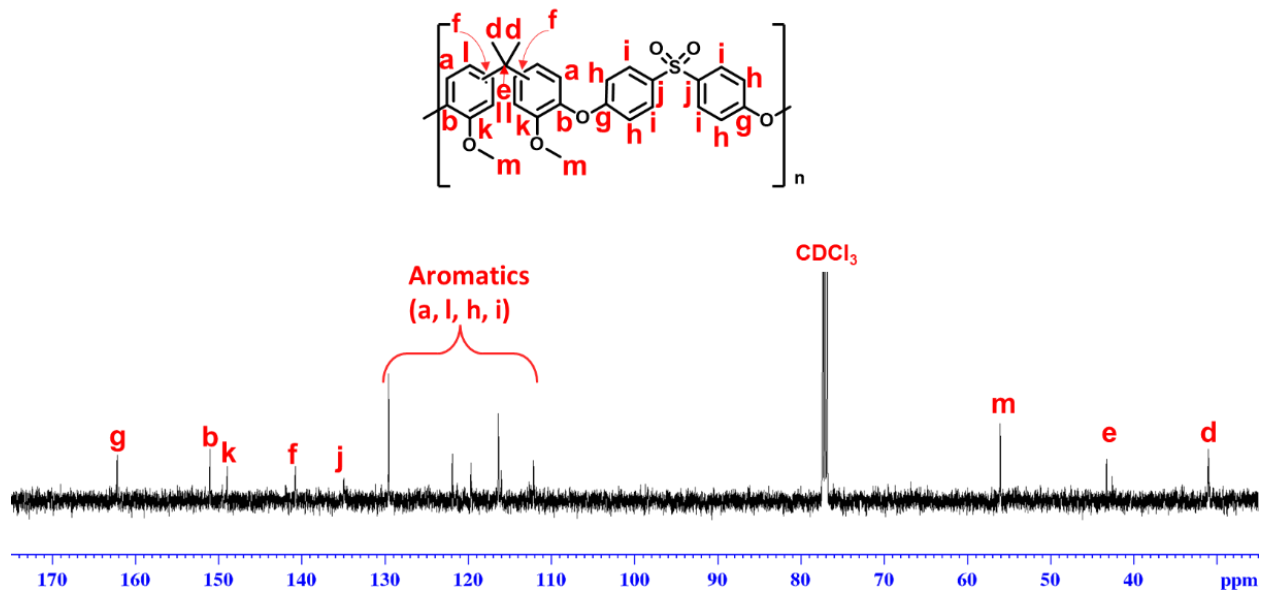


Figure S6. ^{13}C NMR spectrum for BPF-PSf

BGA-PSf: ^1H NMR (500 MHz, CDCl_3) δ 7.81 (dt, $J = 6.7, 3.2$ Hz, 4H), 7.21 – 6.61 (m, 9H), 3.88 – 3.61 (m, 5H), 1.82 – 1.49 (m, 6H). (**Figure S7**)



BGA-PSf: ^{13}C NMR (500 MHz, CDCl_3). (**Figure S8**)



BGF-PSf: ^1H NMR (500 MHz, CDCl_3) δ 7.82 (dd, $J = 16.8, 8.7$ Hz, 4H), 7.22 – 6.70 (m, 10H), 4.09 – 3.45 (m, 8H). (**Figure S9**)

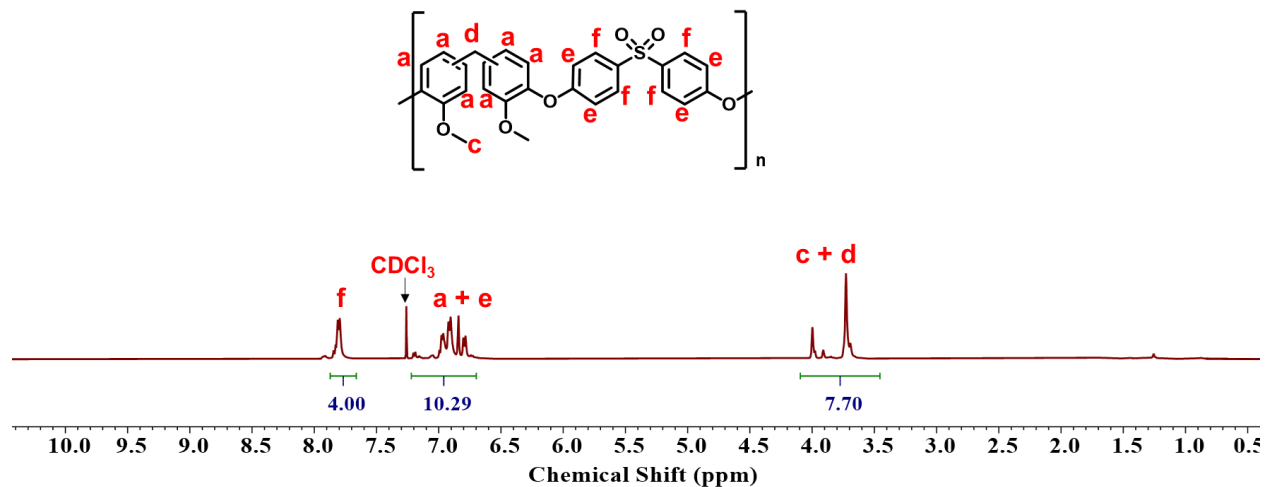


Figure S9. ^1H NMR spectrum for BGF-PSf

BGF-PSf: ^{13}C NMR (500 MHz, CDCl_3). (**Figure S10**)

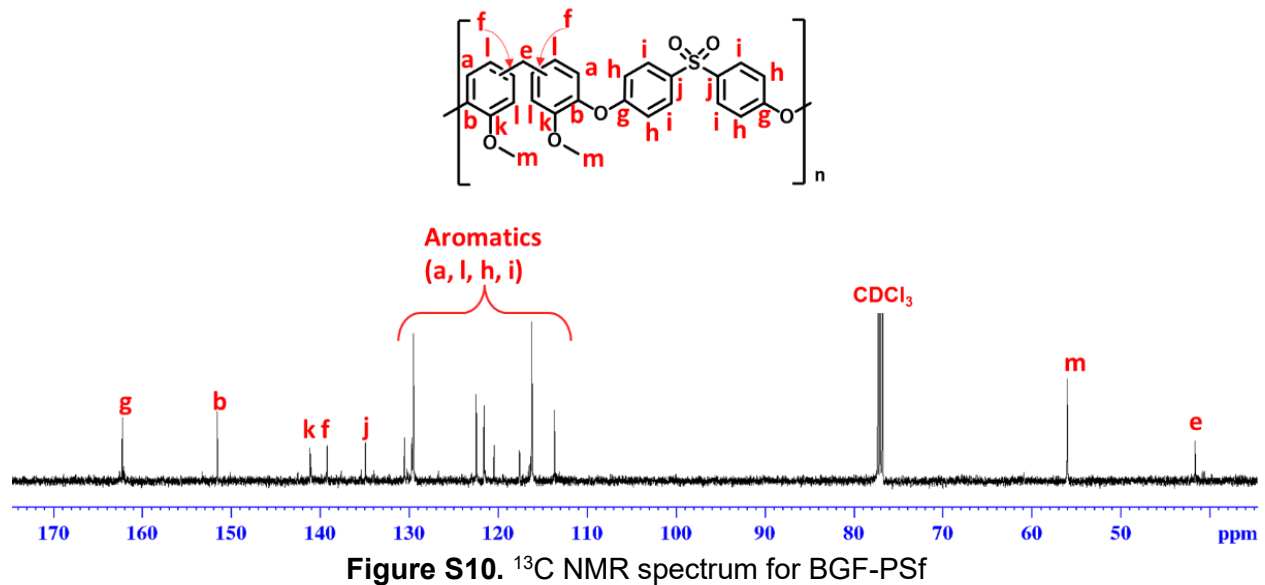


Figure S10. ^{13}C NMR spectrum for BGF-PSf

3. Characterization

3.1 ^1H NMR spectroscopy:

- **Lignin-derivable bisguaiacols:** BGA and BGF samples were prepared in CDCl_3 and analyzed on a Bruker AVIII 600 MHz spectrometer. ^1H NMR spectra were analyzed using the MestReNova v1.8 software package.
- **PSfs:** All PSf NMR samples were prepared in CDCl_3 and analyzed using a Bruker Ascend 500 MHz spectrometer. ^1H and ^{13}C NMR spectra were analyzed using the TopSpin v4.3.0 software package.

3.2 Mass spectrometry: The exact molar masses of the bisguaiacols were determined by FTMS (ESI) using a Q-Exactive Orbitrap (Thermo Fisher Scientific) mass spectrometer. The respective compound was dissolved in acetonitrile (~ 0.1 mg/mL), for the FTMS (ESI) experiments, which were conducted in positive ion mode by direct syringe injection of samples.

3.3 Size exclusion chromatography (SEC): SEC was performed using a Waters Alliance e2695 HPLC system connected to a Wyatt Optilab T-rEX differential refractive index (dRI) detector. Two WatersTM Styragel[®] HR 5 THF and Styragel[®] HR 4 THF columns were used in series. This setup was linked to Astra v6.1 software, which was used for the analysis. The mobile phase was THF OptimaTM with a flow rate of 1 mL/min and an injection volume of 100 μL . A calibration curve was made using five low-dispersity polystyrene (PS) samples with mid-point molecular weights (M_p s) of 9.82, 30.00, 91.45, 200.00, and 482.00 kDa. PS standards (30.00 and 200.00 kDa) were acquired from Pressure Chemical Company, and the rest of the standards (9.82, 91.45, and 482.00 kDa) were purchased from Agilent Technologies. The SEC samples were prepared by dissolving PSfs in THF OptimaTM at ~ 5 mg/mL (at 23 $^\circ\text{C}$). The samples were filtered using a Spectrum 0.22- μm PTFE syringe filter. The PSfs exhibited number-average molecular weights (M_n s) between 14.5 and 48.0 kDa and dispersities between 1.6 and 3.4 (**Figure S11**).

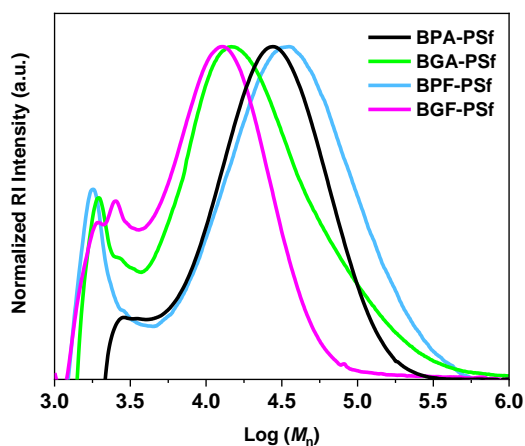


Figure S11. Normalized RI intensity as a function of logarithmic molar mass (M_n) measured via SEC for PSfs.

3.4 Fabrication of lignin-derivable PSf membranes: Dense membranes were fabricated to compare the hydrophilicity of the PSfs *via* water contact angle measurements. The dried PSfs were dissolved in DMF at 2.5 w/w%. The PSf solution was then filtered using a 0.45- μ m PTFE syringe filter and poured into a VWR petri dish (diameter \sim 10 cm). The dish was covered with a loosely fitted lid and left at \sim 23 °C for 24 h in a fume hood. DMF was then gradually removed by placing the uncovered petri dish in a vacuum oven (Fisherbrand Isotemp Model 281A) at: 23 °C, 40 °C, 100 °C, and 160 °C, each for a 24 h period. Next, the dried dense membranes were removed from the petri dish by adding DI water, allowing the membrane to swell, and then gently peeling it off. The membranes were dried under vacuum at 160 °C for 14 h in a glass vial. The dried polymer films were transparent, with a smooth surface. Finally, membranes were taped to a glass slide, prior to contact angle measurements.

3.5 Water contact angle measurements: The water contact angle measurements were performed using a Ramé-hart automated goniometer (Model 230-U1) equipped with a microscope and an illumination system. DROPimage Advanced[®] software (v2.7.03) was used for data interpretation. Approximately 5 μ L of DI water was deposited onto the dried PSf dense membranes, which were attached to glass slides with Scotch[™] tape, using a Hamilton (model 1750TPLT) Luer tip threaded plunger syringe and a 16-gauge stainless steel blunt needle. For these measurements, 6 different areas on each membrane were tested thrice, and the values reported were the average of the data (**Figure S12**).

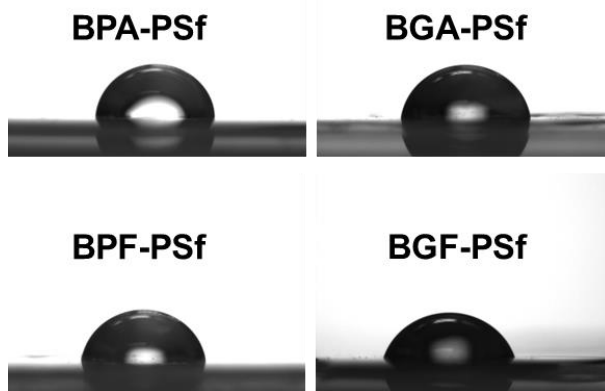


Figure S12. Water contact angle images for dense membranes of BPA/BGA/BPF/BGF-PSfs.

3.6 Solubility parameter estimations: The solubility parameters for PSfs were calculated from group contributions using the Hoftyzer and van Krevelen method (**Table S1**).⁶ The following equations were used for the calculations.

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad \dots\dots\dots(1)$$

$$\delta_d = \frac{\sum F_{di}}{V} \quad \dots\dots\dots(2)$$

$$\delta_p = \frac{\sqrt{\sum F_{pi}^2}}{V} \quad \dots\dots\dots(3)$$

$$\delta_h = \frac{\sqrt{\sum E_{hi}}}{V} \quad \dots\dots\dots(4)$$

Wherein - δ : total solubility parameter, δ_d : square root of energy density associated with dispersion forces, δ_p : square root of energy density associated with dipolar intermolecular forces, δ_h : square root of energy density associated with hydrogen-bonding interactions between molecules, F_{di} : dispersion component of an individual structural group, F_{pi} : polar component of an individual structural group, E_{hi} : hydrogen bonding energy of an individual structural group, and V: molar volume.

Table S1. Solubility parameters for BPA/BGA/BPF/BGF-PSfs.

	Polymer	Methoxy groups	δ_p (MPa ^{1/2})	δ_d (MPa ^{1/2})	δ_h (MPa ^{1/2})	δ (MPa ^{1/2})
Dimethyl-substituted bridging carbon	BPA-PSf	0	4.0	18.5	4.7	19.5
	BGA-PSf	2	4.2	21.1	6.2	22.4
Unsubstituted bridging carbon	BPF-PSf	0	4.4	18.9	4.9	20.0
	BGF-PSf	2	4.6	21.7	6.5	23.1

3.7 Surface free energy measurements: The determination of surface free energy was conducted using the extended Fowkes method, which separates the surface energy into polar and dispersive components.^{7, 8} The contact angles of two liquids, one polar and one non-polar, were measured, and along with the known surface tension of both liquids, the polar and dispersive surface energy components of the membranes were derived. The tests were carried out with a Ramé-hart automated goniometer (Model 230-U1). DROPimage Advanced[®] software (v2.7.03) was employed to interpret the data. DI water was used to assess the polar component, and diiodomethane was used to assess the dispersive component. The total surface free energy was

then computed by summing the contributions from both polar and dispersive components. Five areas were selected on each membrane for measurement, and every PSf membrane was tested thrice. The reported data (**Table S2**) were the average of these measurements.

Table S2. Surface energy for BPA/BGA/BPF/BGF-PSfs.

	Polymer	Methoxy groups	Polar component (mJ/m ²)	Dispersive component (mJ/m ²)	Total surface energy (mJ/m ²)
Dimethyl-substituted bridging carbon	BPA-PSf	0	1.8 ± 0.2	40.3 ± 0.9	42.2 ± 0.8
	BGA-PSf	2	2.6 ± 0.1	42.3 ± 0.1	44.9 ± 0.2
Unsubstituted bridging carbon	BPF-PSf	0	2.1 ± 0.1	45.5 ± 0.3	47.6 ± 0.3
	BGF-PSf	2	5.6 ± 0.2	42.1 ± 0.3	47.7 ± 0.3

3.8 Octanol-water partition coefficient (log P) estimations: The log P values of bisphenols/bisguaiacols were estimated using an online platform <http://chemicalize.org> by ChemAxon 2024,⁹ which displays atoms in MarvinSpace. The chemical structure of each individual compound (BPA, BPF, BGA, and BGF) was input into the online platform, and the respective log P value for the bisphenol/bisguaiacol was generated (**Table S3**).

Table S3. Log P values for BPA/BGA/BPF/BGF.

	Bisphenol	Methoxy groups	Log P
Dimethyl-substituted bridging carbon	BPA	0	4.0
	BGA	2	3.7
Unsubstituted bridging carbon	BPF	0	3.4
	BGF	2	3.1

3.9 Water vapor uptake: The water vapor sorption properties of PSf dense membranes were measured using a Q5000 sorption analyzer from TA Instruments. For these tests, 5 - 15 mg of dense membrane was placed in quartz pans. The experiments were carried out under an UHP N₂ atmosphere. The protocol involved maintaining a relative humidity (RH) of 0% and waiting until a weight change was less than 0.01% for 5 min, followed by adjusting the RH to 95% until the weight change remained below 0.01% for 5 min. For each PSf, triplicates were tested, and the average increase in weight was recorded as the water vapor uptake of the membranes.

3.10 Differential scanning calorimetry (DSC): The glass transition temperatures (T_g s) of PSfs were determined using a Q2000 calorimeter from TA Instruments. Samples (~5 mg) were loaded into non-hermetically sealed aluminum pans. The pans were heated to 190 °C at a rate of 10 °C/min in a N₂ atmosphere and held at 190 °C for 10 min. The samples were then cooled to -80 °C at a rate of 10 °C/min under a N₂ atmosphere and held at -80 °C for 10 min. The samples were again heated to 200 °C at the same rate. The T_g values were reported as the midpoint of the inflection from the second heating scan, which was estimated using TA Instruments Universal Analysis 2000 software (v4.5A) (**Figure S13**).

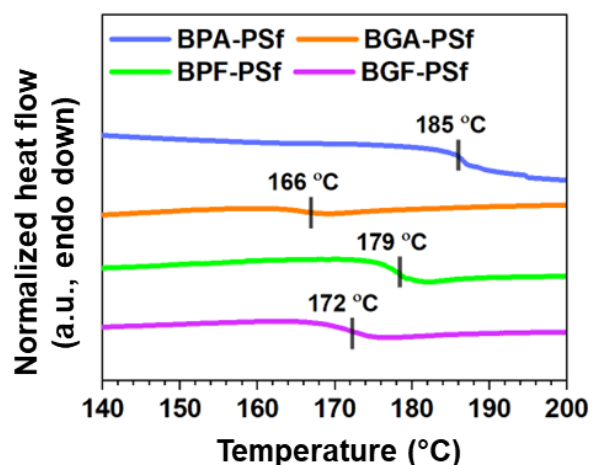


Figure S13. Representative DSC second heating traces of BPA/BGA/BPF/BGF-PSfs.

3.11 Thermogravimetric analysis (TGA): The degradation temperatures of the synthesized PSfs were analyzed using a TGA 5500 from TA Instruments. About ~5 mg of the respective PSf was placed in a high-temperature platinum pan. The pan was heated to 175 °C at 10 °C/min in a N₂ environment to evaporate residual moisture or solvents that may have been present. Then, the pan was cooled to 40 °C and re-heated to 800 °C at 10 °C/min under an N₂ flow. The degradation temperatures of the PSfs were reported as the temperature at which a 5 wt% loss was noted.

Abbreviations

BGA	bisguaiacol A
BGF	bisguaiacol F
BPA	bisphenol A
BPF	bisphenol F
DCM	dichloromethane
DFDPS	4,4'-Difluorodiphenyl sulfone
DI	deionized
DMAc	<i>N,N</i> -dimethylacetamide
DMF	<i>N,N</i> -dimethylformamide
DMSO	dimethyl sulfoxide
DMSO- <i>d</i> ₆	deuterated dimethyl sulfoxide
DSC	differential scanning calorimetry
E_{hi}	hydrogen bonding energy of an individual structural group
ESI	electrospray ionization
F_{di}	dispersion component of an individual structural group
F_{pi}	polar component of an individual structural group
FTMS	Fourier transform mass spectrometry
log P	octanol-water partition coefficient
M_n	number-average molecular weight
M_p	midpoint molecular weight
NMR	nuclear magnetic resonance
PS	polystyrene
PSf	polysulfone
RH	relative humidity
RI	refractive index
SEC	size exclusion chromatography
$T_{d5\%}$	temperature of 5% weight loss
T_g	glass transition temperature
THF	tetrahydrofuran
TGA	thermogravimetric analysis
V	molar volume
δ	total solubility parameter
δ_d	square root of energy density associated with dispersion forces
δ_p	square root of energy density associated with dipolar intermolecular forces
δ_h	square root of energy density associated with hydrogen-bonding interactions between molecules

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