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

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The functionality inherent in lignin-derivable aromatics (*e.g.*, polar methoxy groups) can provide a potential opportunity to improve the hydrophilicity of polysulfones (PSfs) without the need for the additional processing steps and harsh reagents/conditions that are typically used in conventional PSf modifications. As determined herein, lignin-derivable PSfs without any post-polymerization modification exhibited higher hydrophilicity than comparable petroleum-based PSfs (commercial/laboratory-synthesized) and also demonstrated similar hydrophilicity to functionalized BPA-PSfs reported in the literature. Importantly, the lignin-derivable PSfs displayed improved thermal properties relative to functionalized BPA-PSfs in the literature, and the thermal properties of these bio-derivable PSfs were close to those of common non-functionalized PSfs. In particular, the glass transition temperature (T_g) and degradation temperature of 5% weight loss ($T_{d5\%}$) of lignin-derivable PSfs (T_g ~165–170 °C, $T_{d5\%}$ ~400–425 °C) were significantly higher than those of typical functionalized BPA-PSfs in the literature (T_g ~110–160 °C, $T_{d5\%}$ ~240–260 °C) and close to those of unmodified, commercial/laboratory-synthesized BPA-/bisphenol F-PSfs (T_g ~180–185 °C, $T_{d5\%}$ ~420–510 °C).

Sustainability spotlight

Commercial bisphenol A-polysulfones (BPA-PSfs) are hydrophobic in nature, and post-polymerization modification is often required to increase the hydrophilicity of commercial PSfs for water filtration applications. Such PSf modification adds extra processing steps and often requires harsh reaction conditions/reagents, and these extra functionalization steps also have a detrimental effect on application-specific thermal properties. Herein, bio-derivable PSfs were synthesized using potentially safer, lignin-derivable bisguaiacols. Notably, the lignin-derivable PSfs, without any post-polymerization modification, demonstrated similar hydrophilicity to functionalized BPA-PSfs reported in the literature, and they also exhibited improved thermal properties relative to functionalized BPA-PSfs. Moreover, the thermal properties of bio-derivable PSfs remained close to those of commercial BPA-PSfs. Overall, this work is aligned with the UN's Sustainable Development Goal 12 (responsible consumption and production of chemicals).

Poly(arylene ether sulfone)s, or polysulfones (PSfs), are a class of engineering polymers widely used in food and beverage processing materials, including water filtration membranes, due to their high-temperature stability, resistance to hydrolysis, and chemical inertness.[1–3] PSfs are hydrophobic in nature, and often post-polymerization functionalization (*e.g.*, chlorination,[4] sulfonation,[5] incorporation of hydrophilic zwitterionic groups[6,7]) is necessary to increase PSf hydrophilicity,[8,9] which also improves water permeability and fouling resistance through the formation of a hydration layer on the PSf membrane.[8] This extra functionalization, however, requires harsh reaction conditions/reagents/toxic solvents, such as concentrated sulfuric acid or chlorinated solvents.[4,5] Additionally, these functionalized PSfs often have significantly reduced thermal properties (*i.e.*, glass transition temperature [T_g] and degradation temperature) in comparison to those of commercial PSfs, as the functionalization modifies the main-chain repeat unit of the polymer (*e.g.*, the introduction of long aliphatic chains and/or thermally less stable linkages/functional groups).[10] Moreover, commercial PSfs are primarily derived from bisphenol A (BPA), a suspected endocrine disruptor.[11,12] A variety of commercial BPA alternatives, such as bisphenol F (BPF), bisphenol S, and tetramethyl BPA, have emerged; however, these alternatives may still have endocrine disruption potential.[11,12] These bisphenols (unreacted and/or oligomers) can leach from polymeric products and potentially enter the human body. An additional concern is that BPA and its commercial analogues are non-renewable.[13,14] Altogether, PSfs

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with increased hydrophilicity *vs.* unmodified BPA-based counterparts, while maintaining thermal properties, are highly desirable.

Lignin is the most abundant source of renewable aromatic chemicals and serves as a platform for the development of an array of sustainable polymers.[15–25] Polymers made from bulk lignin typically have inconsistent thermomechanical properties due to structural heterogeneity and limited reactivity of lignin;[16,26] however, bulk lignin can be deconstructed into substituted phenols with several inherent functional groups (*e.g.*, methoxy groups) to mitigate this issue.[16,26–28] These substituted phenols have been recently used to generate BPA mimics for epoxy–amine resins,[29] isocyanate-free polyurethanes,[30,31] and polycarbonates[32] with highly tunable thermomechanical properties. Additionally, several studies have suggested that these materials have reduced toxicity concerns (*e.g.*, estrogenic activity, genotoxicity, oxidative DNA damage) relative to their BPA-/BPF-based counterparts.[11,33,34]

Herein, lignin-derivable PSfs were synthesized from these bio-derivable bisguaiacols. The water contact angle (θ_w), water vapor uptake, and thermal properties of these bisguaiacol-based PSfs were benchmarked against laboratory-synthesized BPA-/BPF-based PSfs, commercial BPA-PSf (Udel® PSU, Solvay),[2] and quaternary ammonium-functionalized BPA-PSfs reported in the literature.[10] It was envisioned that the polar methoxy groups on lignin-derivable bisguaiacols would improve the hydrophilicity of resultant polymers without the need for any post-polymerization functionalization.[35] Additionally, the thermal properties (T_g and

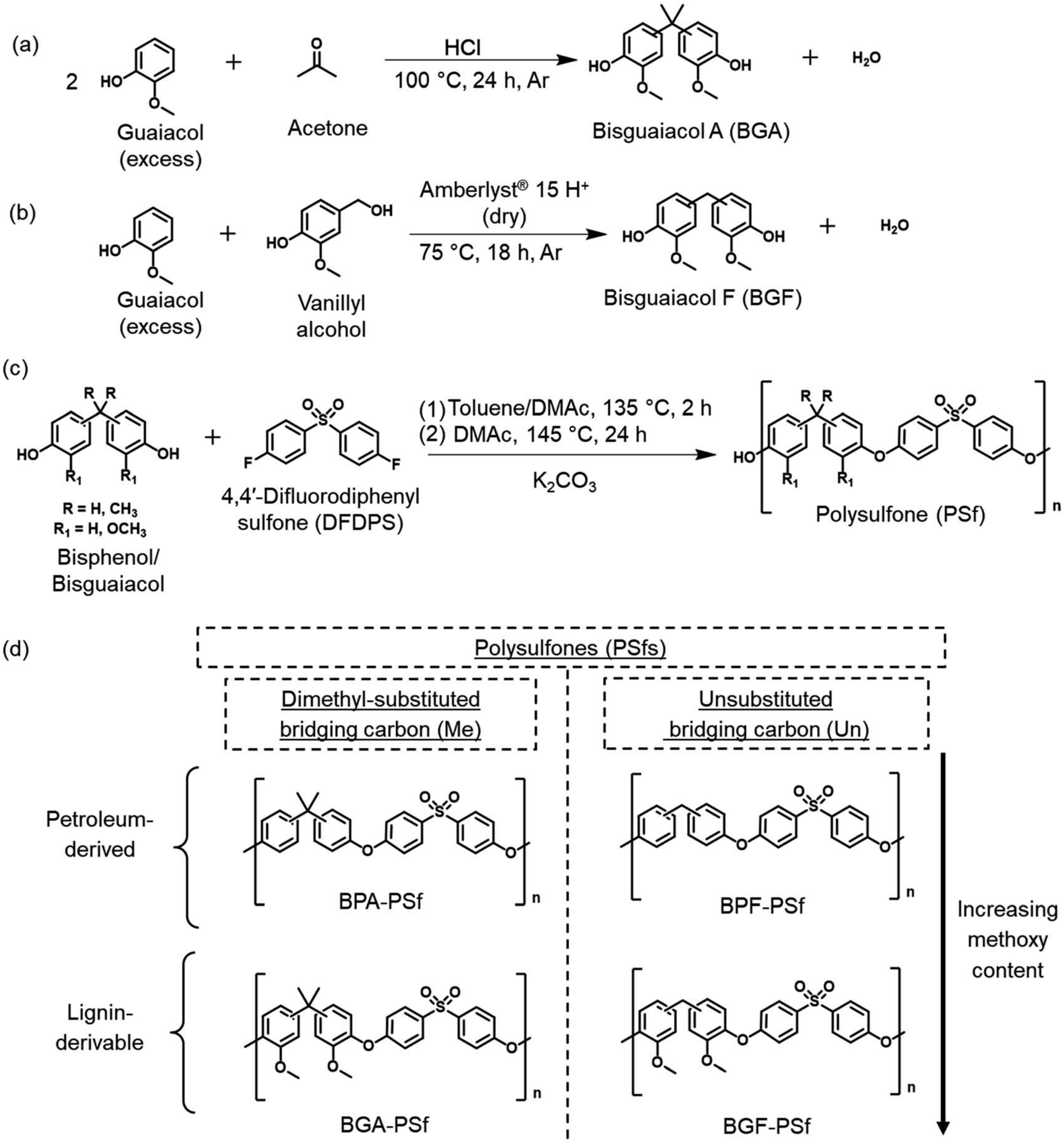

Fig. 1 (a) Synthesis of regioisomeric BGA using guaiacol and acetone. (b) Synthesis of regioisomeric BGF using guaiacol and vanillyl alcohol. (c) Synthesis of PSf from respective bisphenol and DFDPS. (d) Molecular structures of synthesized PSfs, wherein the petroleum-derived analogues, BPA/BPF-PSfs (on the top), have no methoxy groups on either ring (0,0), and the lignin-derivable, BGA/BGF-PSfs (on the bottom) have two methoxy groups, one on the right-most and one on the left-most bisphenol aromatic ring (1,1).

degradation temperature) of these lignin-derivable PSfs were expected to be comparable to those of the unmodified, commercial PSfs due to their structural similarity.[35]

Lignin-derivable bisguaiacol A (BGA) and bisguaiacol F (BGF) were synthesized as analogues to BPA and BPF to achieve the above objective. BGA was synthesized *via* the electrophilic aromatic condensation between guaiacol and acetone.[30] The reaction was conducted in an excess of guaiacol to minimize by-product formation from the self-condensation of acetone (Fig. 1a).[31,35,36] BGA contains a dimethyl-substituted bridging carbon (*i.e.*, isopropylene bridge) between the two aromatic moieties and more closely resembles BPA.[30] BGF was synthesized *via* the electrophilic aromatic substitution between guaiacol and vanillyl alcohol (Fig. 1b), and the direct condensation approach eliminated the need for formaldehyde, which is prominent in BPF production.[29,37] BGF has an unsubstituted bridging carbon (*i.e.*, methylene bridge), which makes it more structurally similar to BPF.[29,37] Detailed BGA/BGF synthesis and purification procedures, along with characterization information (Fig. S1 and S2†), can be found in the ESI.†

PSfs were subsequently synthesized *via* standard step-growth polymerization[38] (Fig. 1c) by reacting the respective bisphenol/bisguaiacol with 4,4′-difluorodiphenyl sulfone. This process involved a nucleophilic aromatic substitution (SnAr) reaction, in which the bisphenolate salts generated through deprotonation using potassium carbonate reacted with the dihalide (4,4′-difluorodiphenyl sulfone) in a polar aprotic solvent, specifically, *N*,*N*-dimethylacetamide (DMAc). The detailed synthetic procedures, polymer isolation/purification protocols, nuclear magnetic resonance spectra (Fig. S3–S10†), and size exclusion chromatography data (Fig. S11†) are provided in the ESI.† The molecular structure of the petroleum-derived PSfs and their lignin-derivable analogues are presented in Fig. 1d.

The hydrophilicity of these bio-derivable PSfs was studied by measuring/estimating θ_w, water vapor uptake, and polymer polarity (Fig. 2 and Table 1). The typical θ_w for commercial BPA-PSf was $\sim$90°,[2,10] which was similar to our laboratory-synthesized BPA-PSf. θ_w for lignin-derivable BGF-PSf was $\sim$75°, which was comparable to that of functionalized BPA-PSfs reported in the literature.[10] Moreover, θ_w decreased (*i.e.*, the hydrophilicity of the PSfs increased) with increasing methoxy content, likely due to the polar nature of methoxy groups in lignin-derivable PSfs (Fig. 2a). For instance, the laboratory-synthesized BPA-PSf (with 0 methoxy groups) had a θ_w of $\sim$90°. In contrast, its lignin-derivable analogue, BGA-PSf (with 2 methoxy groups), had a θ_w of $\sim$81°. Similarly, BPF-PSf (with 0 methoxy groups) had a θ_w of $\sim$84°, whereas its lignin-derivable counterpart, BGF-PSf (with 2 methoxy groups), had a θ_w of $\sim$75°. Hence, the methoxy moieties on lignin-aromatics appear to improve the hydrophilicity of PSfs.

The water vapor uptake of PSfs also increased with the number of methoxy groups (Fig. 2b). For example, laboratory-synthesized BPA-PSf (with 0 methoxy groups) exhibited a water vapor uptake of $\sim$0.9% (comparable to that of commercial BPA-PSf, $\sim$0.8%),[2] whereas BGA-PSf (with 2 methoxy groups) had a water vapor uptake of $\sim$1.3%. This improvement was statistically significant (paired T-test, *p*-value = 0.048), indicating $\sim$50% higher water vapor uptake for BGA-PSf *vs.* BPA-PSf. BPF-PSf (with 0 methoxy groups) had a water vapor uptake of $\sim$1.0% and BGF-PSf (with 2 methoxy groups) had a water vapor uptake of $\sim$1.1%. This increase in water vapor uptake did not reach statistical significance (paired T-test, *p*-value = 0.080). Nonetheless, these lignin-derivable PSfs, which do not require the harsh reagents or conditions typically associated with PSf modifications, yield materials with improved water vapor uptake within the experimental constraints of dense film matrices.[6,10]

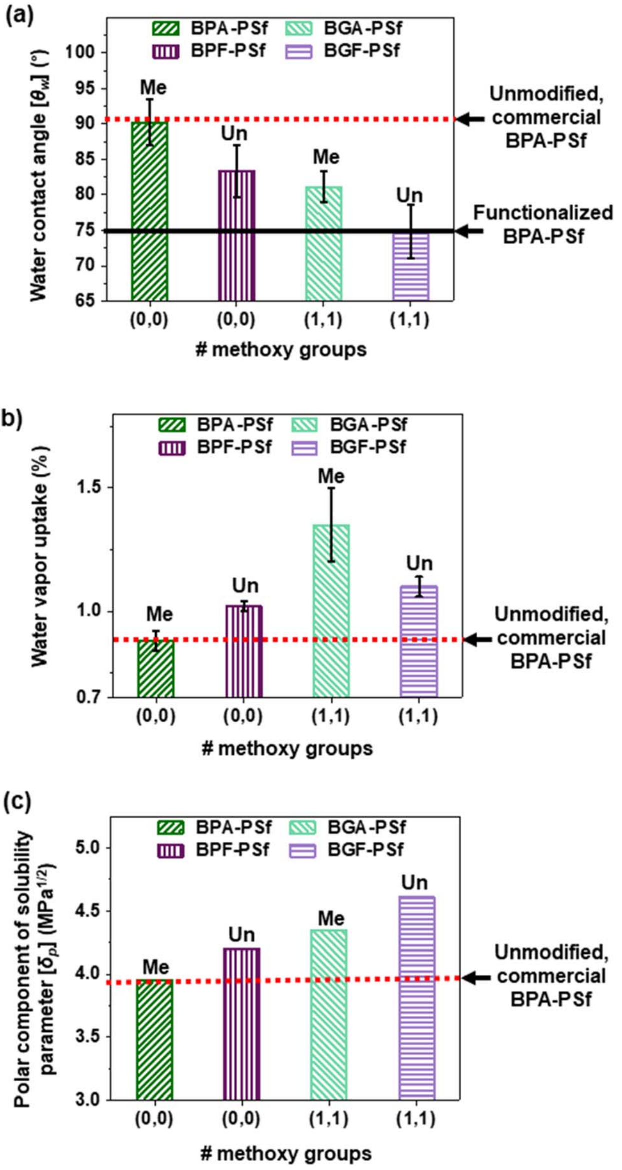

Fig. 2 (a) θ_w, (b) water vapor uptake, and (c) δ_p values as a function of methoxy groups on the aromatic rings for laboratory-synthesized BPA/BGA/BPF/BGF-PSfs. The bar label indicates the bridging-carbon substitution type for the PSfs. The red dashed line represents a reported value (θ_w $\sim$90°, water vapor uptake $\sim$0.8%, polar component of solubility parameter $\sim$3.9) for unmodified, commercial BPA-PSf [Udel® PSU, Solvay],[2] whereas the black solid line in panel (a) indicates an average reported value in the literature (θ_w $\sim$75°) for functionalized BPA-PSf.[10]

Table 1 Characterization summary of PSfs[a]

	Polymer	Methoxy groups	θ_w	T_g	$T_{d5\%}$	Char content[b]
Commercial PSf (Solvay[2])	BPA-PSf	0	91 ± 2°	185 °C	510 °C	31%
Petroleum-based PSfs (laboratory-synthesized)	BPA-PSf	0	90 ± 3°	185 °C	510 °C	31%
	BPF-PSf	0	84 ± 3°	179 °C	420 °C	44%
Functionalized PSfs (from literature[10])[c]	BPA-PSf	0	77 ± 3°	164 °C	240 °C	28%
	BPA-PSf	0	71 ± 2°	127 °C	260 °C	30%
	BPA-PSf	0	75 ± 6°	112 °C	255 °C	21%
Lignin-derivable PSfs (laboratory-synthesized)	BGA-PSf	2	81 ± 2°	166 °C	425 °C	25%
	BGF-PSf	2	74 ± 3°	172 °C	400 °C	46%

[a] Chemical structures of the polymers are provided in Fig. 4. [b] Determined by thermogravimetric analysis from 40 °C to 800 °C at 10 °C min^{-1} in an N_2 atmosphere. [c] Quaternary ammonium-functionalized BPA-PSfs with varying mole fractions (25, 50, 75 mol%) of ammonium charge content, which were synthesized in four steps (as reported in the literature).[10]

The methoxy groups on the aromatic rings in the lignin-derivable PSfs also increased the polymer polarity, consequently improving PSf hydrophilicity. This increase in the polar properties was determined *via* (1) solubility parameter calculations [using the Hoftyzer and van Krevelen method],[39] (2) surface energy estimations [using the extended Fowkes method],[40] and (3) octanol–water partition coefficient (log P) predications [using ChemAxon 2024].[41] For the solubility parameter calculations, δ is the total solubility parameter, δ_d indicates the square root of energy density associated with dispersion forces, δ_p represents the square root of energy density associated with dipolar intermolecular forces, and δ_h is the square root of energy density associated with hydrogen-bonding interactions between molecules.[39] Notably, δ_p increased with the number of methoxy groups on the PSfs (Fig. 2c and Table S1†), which strongly suggested that the methoxy groups were responsible for the improved polarity of lignin-derivable PSfs *vs.* BPA-/BPF-based analogues. These findings were supported by the subsequent analysis of surface energy measurements (details in ESI [Section 3.7]†); an increase in the polar component was noted with increasing methoxy content, directly attributable to the polarity introduced by the methoxy groups (Table S2†). Lastly, the log P values reflected the hydrophilicity of the bisphenols/PSfs, and more negative log P values indicated reduced hydrophilicity.[42,43] The log P values decreased with increasing methoxy content on bisphenols (Table S3†), which again suggested that the methoxy groups accounted for the higher hydrophilicity in the bio-derivable systems. Overall, the methoxy moieties offered improved polarity *vs.* their non-methoxy-containing, petroleum-derived counterparts.

Lignin-derivable PSfs offer a sustainable alternative to traditional BPA-/BPF-derived PSfs for potential water filtration applications (*e.g.*, support for reverse osmosis membranes, microfiltration membranes). As determined herein, methoxy-containing, bisguaiacol-derived PSfs demonstrated improved hydrophilicity relative to neat/unmodified BPA-/BPF-PSfs. This increased hydrophilicity can lead to improved water permeability and filter efficiency, which can result in more effective contaminant removal and reduced fouling of the membranes.[5] For instance, in reverse osmosis processes, despite nearing the theoretical minimum energy requirements for water separation, overall energy demands remain high due to membrane limitations and the need for extensive pretreatment.[44] The performance of such membranes can be improved by increasing their

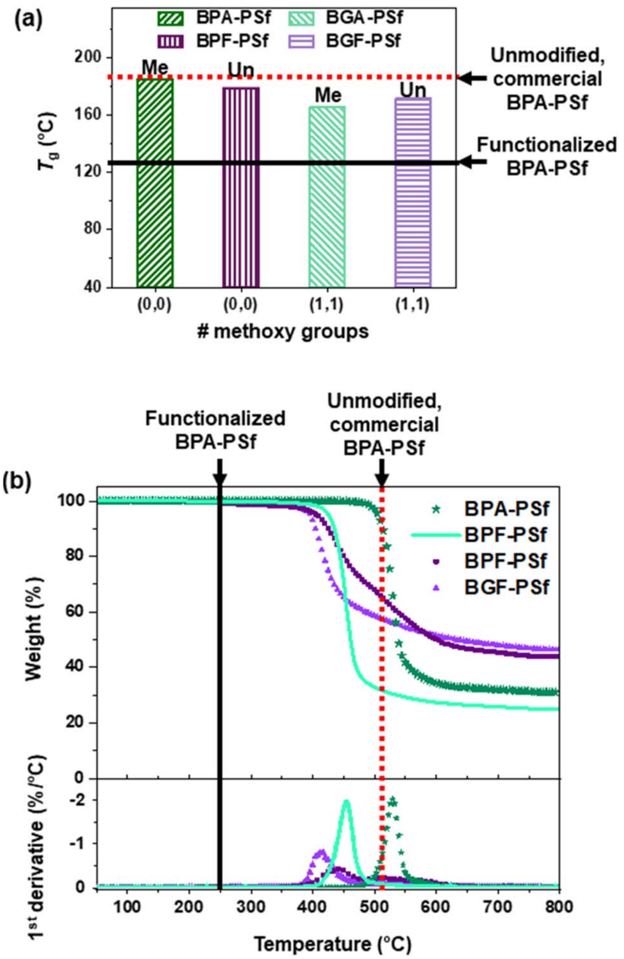

Fig. 3 (a) T_g for laboratory-synthesized BPA/BGA/BPF/BGF-PSfs. (b) Representative thermogravimetric analysis traces and the respective first-derivative curves of sample mass remaining *versus* temperature for laboratory-synthesized BPA/BGA/BPF/BGF-PSfs obtained at a heating rate of 10 °C min^{-1} in an N_2 atmosphere. The red dashed line represents a reported value (T_g ~185 °C, $T_{d5\%}$ ~510 °C) for unmodified, commercial BPA-PSf [Udel® PSU, Solvay],[2] whereas the black solid line indicates an average reported value in the literature (T_g ~130 °C, $T_{d5\%}$ ~250 °C) for functionalized BPA-PSf.[10]

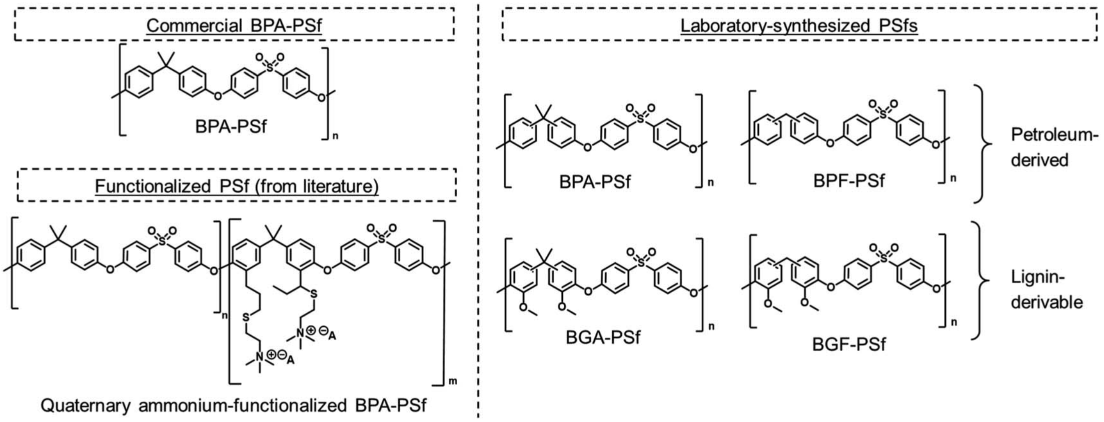

Fig. 4 Molecular structures of commercial, functionalized, and synthesized PSfs.

hydrophilicity, which can reduce total energy consumption/operational costs and make desalination processes more energy efficient.[45] In addition to performance enhancement, filtration membranes generated using lignin-aromatics can lead to potential improvement in life-cycle assessment, which can reduce environmental impacts across the product lifetime.[46]

It is worth noting that the T_gs of these lignin-derivable PSfs were close to those of petroleum-derived (commercial/laboratory-synthesized) benchmarks, and these T_gs were much higher than those of functionalized BPA-PSfs reported in the literature (Fig. 3a and Table 1). The T_g values for unmodified, commercial and laboratory-synthesized BPA-PSf were identical (∼185 °C),[2] and the T_g value for laboratory-synthesized BPF-PSf was ∼179 °C. The T_gs of our lignin-derivable BGA-PSf and BGF-PSf were 166 °C and 172 °C, respectively, whereas the T_gs of several functionalized BPA-PSfs reported in the literature were ∼112 °C, 127 °C, and 164 °C (Fig. 3a).[10] Importantly, in lignin-derivable PSfs, the polymer repeat unit was retained in contrast to the functionalized PSfs in the literature, and thus, the T_gs of lignin-derivable BGA-/BGF-PSfs were close to those of unmodified, commercial and laboratory-synthesized BPA-/BPF-PSfs. The T_gs of lignin-derivable BGA-/BGF-PSfs were slightly lower than those of BPA-/BPF-PSfs, which may be due to less efficient chain packing caused by methoxy groups.[29,31] Notably, the T_g values for lignin-derivable PSfs are more than sufficient for potential applications, such as water filtration membranes, microwaveable dishes, and hemodialysis membranes.[6,7]

The thermal degradation temperatures of these bisguaiacol-based PSfs also were in the range of high-performance thermoplastics. The $T_{d5\%}$ (*i.e.*, temperature of 5% weight loss in an N_2 atmosphere) values for commercial and laboratory-synthesized BPA-PSf were equivalent (∼510 °C),[2] and the $T_{d5\%}$ value for BPF-PSf was ∼420 °C. The $T_{d5\%}$ values for our laboratory-synthesized BGA-PSf and BGF-PSf were 425 °C and 400 °C, respectively (Fig. 3b and Table 1), whereas $T_{d5\%}$ values for several functionalized BPA-PSfs reported in the literature were ∼240 °C, 255 °C, and 260 °C.[10] It is hypothesized that the lignin-derivable PSfs, were more thermally stable than the functionalized PSfs reported in the literature, likely due to the retention of the polymer repeat unit in contrast to the functionalized PSfs. Additionally, all PSfs exhibited a char content of ∼25–45% (Table 1) as these materials typically undergo pyrolysis under an inert atmosphere that leads to char formation rather than oxidative degradation.[47] Overall, the bisguaiacol-based PSfs exhibited significantly higher thermal stability than those of functionalized BPA-PSfs in the literature and similar thermal/char behavior to unmodified materials.

Conclusions

This work highlights the importance of the inherent functionality (methoxy groups) of lignin-aromatics in improving the hydrophilicity of PSfs. The bisguaiacol-based PSfs without any post-polymerization functionalization exhibited equivalent hydrophilicity (θ_w ∼75°) to functionalized PSfs in the literature and higher hydrophilicity than petroleum-based, unmodified, commercial/laboratory-synthesized PSfs (θ_w ∼90°). Notably, θ_w decreased (*i.e.*, the hydrophilicity of the PSfs increased) with increasing methoxy content due to the polar nature of the methoxy groups in lignin-derivable PSfs. Furthermore, these bisguaiacol-based PSfs (T_g ∼165–170 °C, $T_{d5\%}$ ∼400–425 °C) had improved thermal properties relative to functionalized PSfs in the literature (T_g ∼110–160 °C, $T_{d5\%}$ ∼240–260 °C). The thermal properties of lignin-derivable PSfs were close to those of commercial PSfs (T_g ∼180–185 °C, $T_{d5\%}$ ∼420–510 °C), which was likely due to the retention of the polymer repeat unit. Together, these bisguaiacol-based PSfs may serve as potential alternatives to BPA-/BPF-based PSfs for water filtration applications.

Abbreviations

BGA	bisguaiacol A
BGF	bisguaiacol F
BPA	bisphenol A
BPF	bisphenol F
DMAc	*N*,*N*-dimethylacetamide
$\log P$	octanol–water partition coefficient
Me	dimethyl-substituted bridging carbon

$T_{d5\%}$	degradation temperature of 5% weight loss
T_g	glass transition temperature
PSf	polysulfone
Un	unsubstituted bridging carbon
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
θ_w	water contact angle

Data availability

The data supporting this article have been included as part of the ESI.†

Author contributions

Conceptualization: J. S. M., H. S. B., M. D. G., L. T. J. K., and T. H. E. Investigation and formal analysis: J. S. M. and H. S. B. Writing (original draft) J. S. M. and H. S. B. Writing (review and editing): J. S. M., H. S. B., M. D. G., L. T. J. K., and T. H. E. Funding acquisition, supervision, and project administration: M. D. G., L. T. J. K., and T. H. E.

Conflicts of interest

M. D. G. is co-founder of NuAria, LLC and owns 50% equity interest in the company. The work of this manuscript is not directly related to the activities of the company.

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