

Supporting Information

A Family of Linear Phenolic Polymers with Controlled Hydrophobicity, Adsorption and Antioxidant Properties

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Tables S1-S3. Specific amounts of monomers and deprotecting agents used for synthesis of antioxidant polymers of targeted compositions.

Table S1. P2H_zHex series and PHex

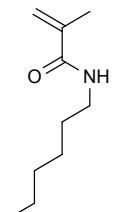
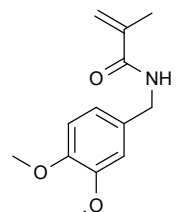
| Targeted molar content, % | Polymerization | | Yield (%) | Deprotection reaction | |
|---------------------------|---|---|-----------|-----------------------|--|
| |  N-hexyl methacrylamide (1) |  N-(3,4-dimethoxybenzyl) methacrylamide (5) | | Polymer | 2M BBr ₃ in CH ₂ Cl ₂ |
| 0 | 1.94 g | - | 88 | - | - |
| 5 | 1.84 g | 0.135 g | 83 | 0.500 g | 0.300 mL |
| 10 | 1.75 g | 0.270 g | 83 | 0.509 g | 0.500 mL |
| 15 | 1.65 g | 0.405 g | 77 | 0.520 g | 0.700 mL |
| 100 | - | 2.70 g | 73 | 0.680 g | 4.50 mL |

Table S2. PBrH_zHex series

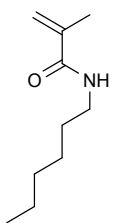
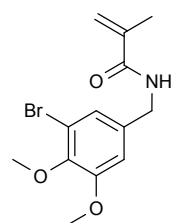
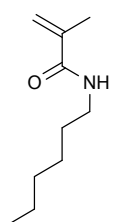
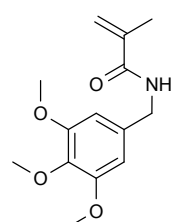
| Targeted molar content, % | Polymerization | | | Deprotection reaction | |
|---------------------------|---|---|-----------|-----------------------|--|
| |  N-hexyl methacrylamide (1) |  N-(3,4-dimethoxy-5-bromobenzyl) methacrylamide (6) | Yield (%) | Polymer | 2M BBr ₃ in CH ₂ Cl ₂ |
| 5 | 1.84 g | 0.180 g | 75 | 0.500 g | 0.300 mL |
| 10 | 1.75 g | 0.361 g | 73 | 0.532 g | 0.500 mL |
| 15 | 1.65 g | 0.541 g | 68 | 0.550 g | 0.700 mL |
| 100 | - | 3.60 g | 59 | 0.910 g | 4.50 mL |

Table S3. P3H_zHex series

| Targeted molar content, % | Polymerization | | | Deprotection reaction | |
|---------------------------|---|--|-----------|-----------------------|--|
| |  N-hexyl methacrylamide (1) |  N-(3,4,5-trimethoxybenzyl) methacrylamide (7) | Yield (%) | Polymer | 2M BBr ₃ in CH ₂ Cl ₂ |
| 5 | 1.84 g | 0.152 g | 81 | 0.503 g | 0.400 mL |
| 10 | 1.75 g | 0.307 g | 79 | 0.517 g | 0.700 mL |
| 15 | 1.65 g | 0.457 g | 82 | 0.530 g | 1.00 mL |
| 100 | - | 3.04 g | 76 | 0.770 g | 6.50 mL |

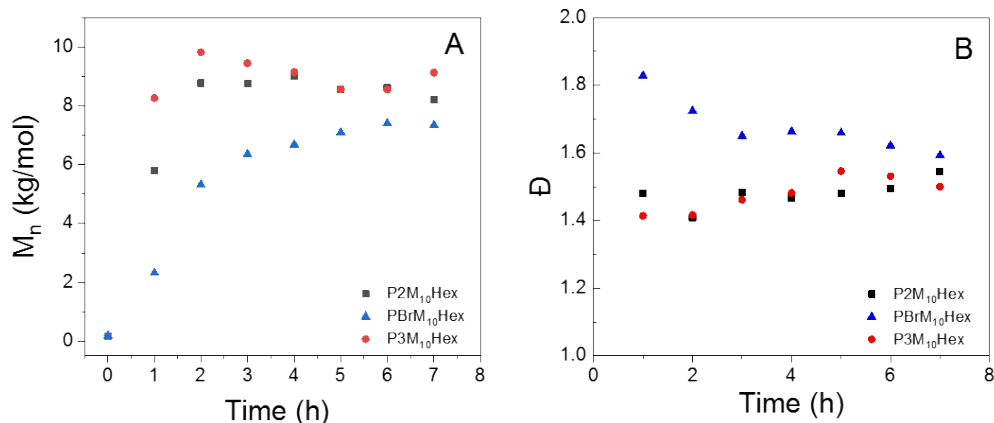


Fig. S1. The number-average molecular weight M_n (A) and molar mass dispersities (B) as a function of polymerization time during synthesis of P2M₁₀Hex, PBrM₁₀Hex, or P3M₁₀Hex at 80°C.

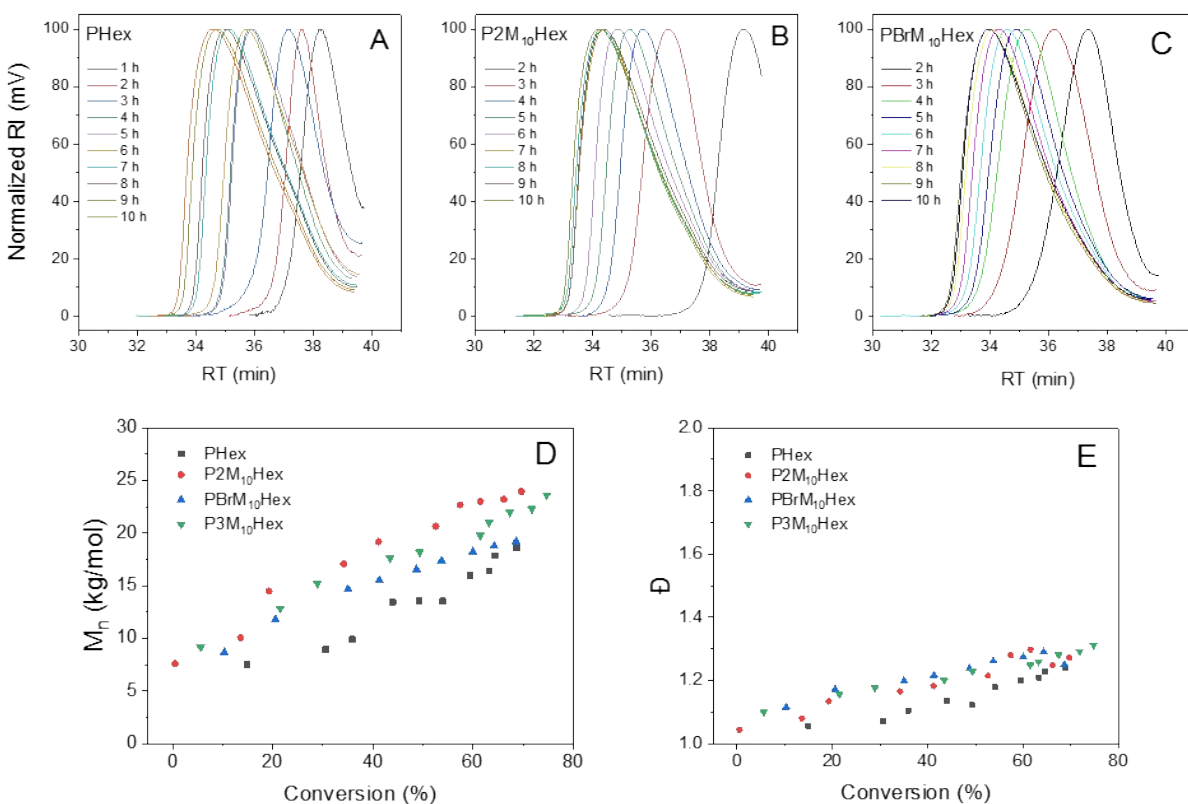


Fig. S2. GPC traces of PHex (A), P2M₁₀Hex (B), PBrM₁₀Hex (C) for different polymerization times, as well as M_n (D) and molar mass dispersities (E) as a function of monomer conversion during polymerization of PHex homopolymer and copolymers containing 10% of phenolic precursor groups at 70°C.

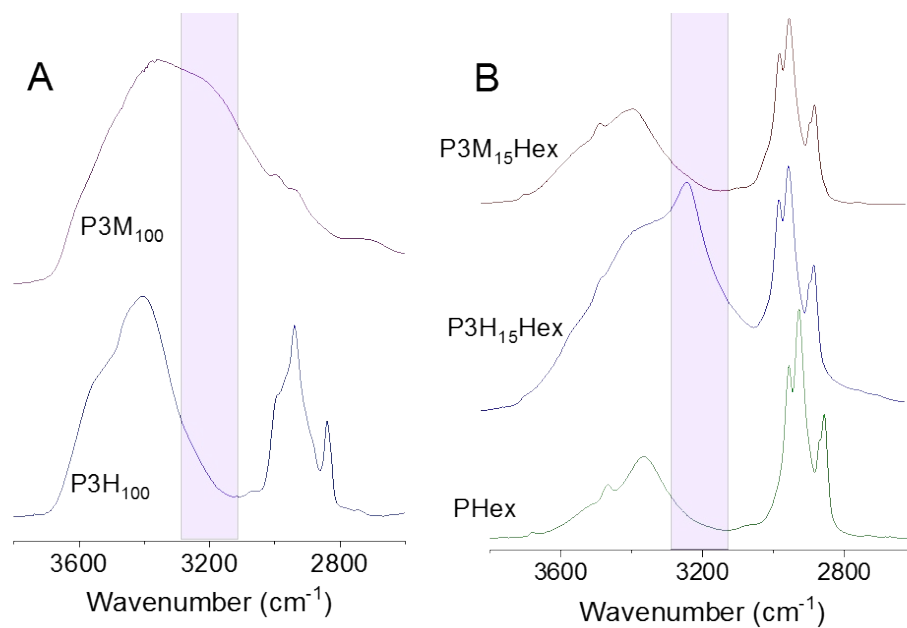


Fig. S3. FTIR spectra of protected and deprotected P3M₁₀₀ and P3H₁₀₀ homopolymers (A), P3M₁₅Hex and P3H₁₅Hex copolymers (B, top) and PHex control polymer (B, bottom).

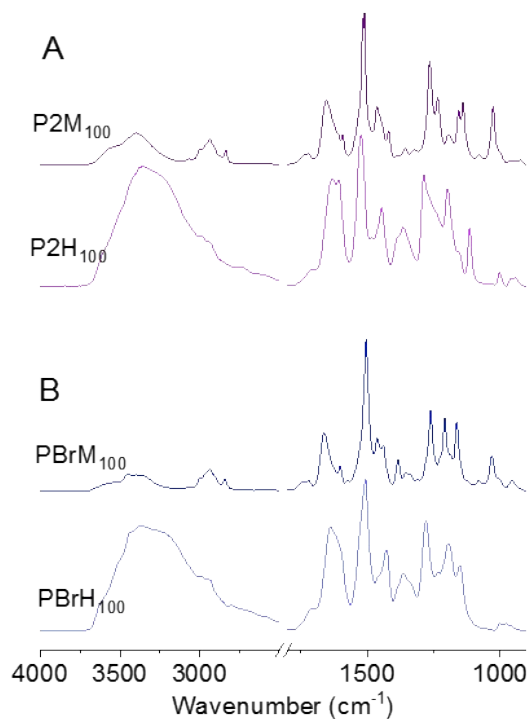


Fig. S4. FTIR spectra of protected and deprotected homopolymers: P2M₁₀₀ and P2H₁₀₀ (A), and PBrM₁₀₀ and PBrH₁₀₀ (B).

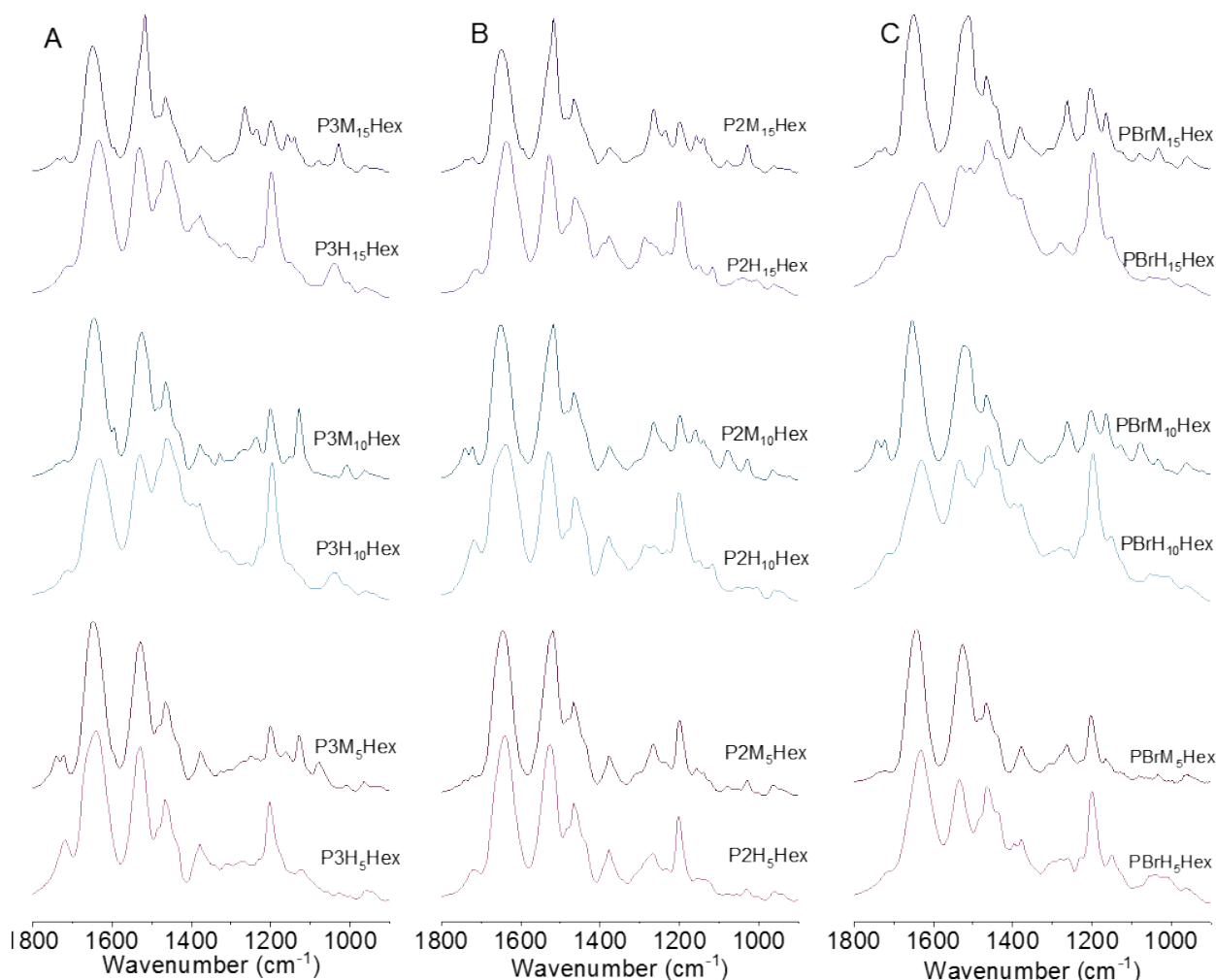


Fig. S5. FTIR spectra of the copolymers of P3M_ZHex and P3H_ZHex series (A), P2M_ZHex and P2H_ZHex series (B), as well as PBrM_ZHex and PBrH_ZHex series (C).

TGA analysis. TGA data indicated the overall similar behavior of all polymers in the temperature range below 200 °C, *i.e.* phenol-containing polymers showed an initial small loss of mass upon heating up to ~100 °C, and retained their mass when further heated to 200°C. Specifically, for homopolymers, the mass loss due to dehydration was ~2, 5, 7 and 10% for PHex, PBrH₁₀₀, P2H₁₀₀, and P3H₁₀₀, respectively. Heating to temperatures significantly higher than 150 °C revealed dramatic differences in the thermal behavior of phenol-containing and phenol-free polymers, as shown in Fig. S6. In particular, phenol-free hexyl homopolymer demonstrated a single wide decomposition step with an onset temperature at 210°C, with the fastest decomposition between

390 °C and 410 °C. In contrast, all phenolic copolymers showed two-step decomposition profiles. The first step in the temperature range between 250 and 300 °C, also seen for phenolic homopolymers, most likely corresponds to crosslinking/decomposition that involves polyphenolic rings. The mass loss of phenolic homopolymers lacked this high-temperature decomposition peak, but instead showed a continuous and gradual mass loss at temperatures between 200 and 500 °C, leaving behind high percentage (42% - 55%) of solid residues after heating to 500 °C.

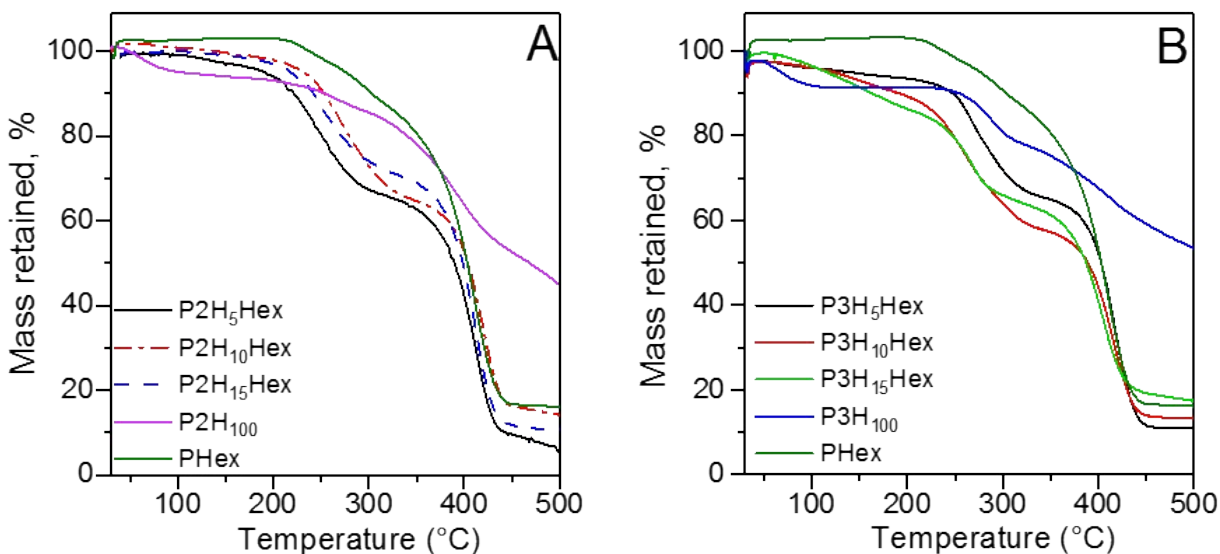


Fig. S6. TGA analysis of P2H_ZHex (A) and P3H_ZHex (B) polymer series.