Title: Turning Renewable Resources into Value-Added Polymer: Development of Lignin-Based Thermoplastic

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Supporting Information

Alternative Synthetic Scheme

To optimize the reaction conditions, an alternative reaction methodology was attempted by combining two reaction steps into one step, i.e., A-Lignin was simultaneously reacted with $PBD(COOH)_2$ and formaldehyde (4 wt% formaldehyde solution, 1.75 mL, 2.3 mmol of formaldehyde) *in situ*. In the first scheme formaldehyde was added at the beginning of the reaction along with all other reagents (*in situ* 1, total 24 h of reaction time). The second scheme consisted of the reaction of A-Lignin with $PBD(COOH)_2$ for 24 h followed by addition of formaldehyde solution and maintaining the reaction condition for an additional 24 h (*in situ* 2, total 48 h of reaction time). Both *in situ* 1 and *in situ* 2 resulted in higher G' than that of A-Lignin-$PBD(COOH)_2$ but not as high as that of W-Lignin-$PBD(COOH)_2$ or F-Lignin-$PBD(COOH)_2$ (**Fig. S1**). This suggests that simultaneous reaction of A-Lignin with $PBD(COOH)_2$ and formaldehyde occurred; however, a significant portion of low molecular weight fraction likely did not crosslink and resulted in poor network formation. It should also be noted that more heterogeneity was observed in the resulting copolymers of *in situ* 1 and *in situ* 2 schemes. A significant amount of insoluble lignin was present due to the prolonged reaction with formaldehyde, which hindered the homogeneous network formation.

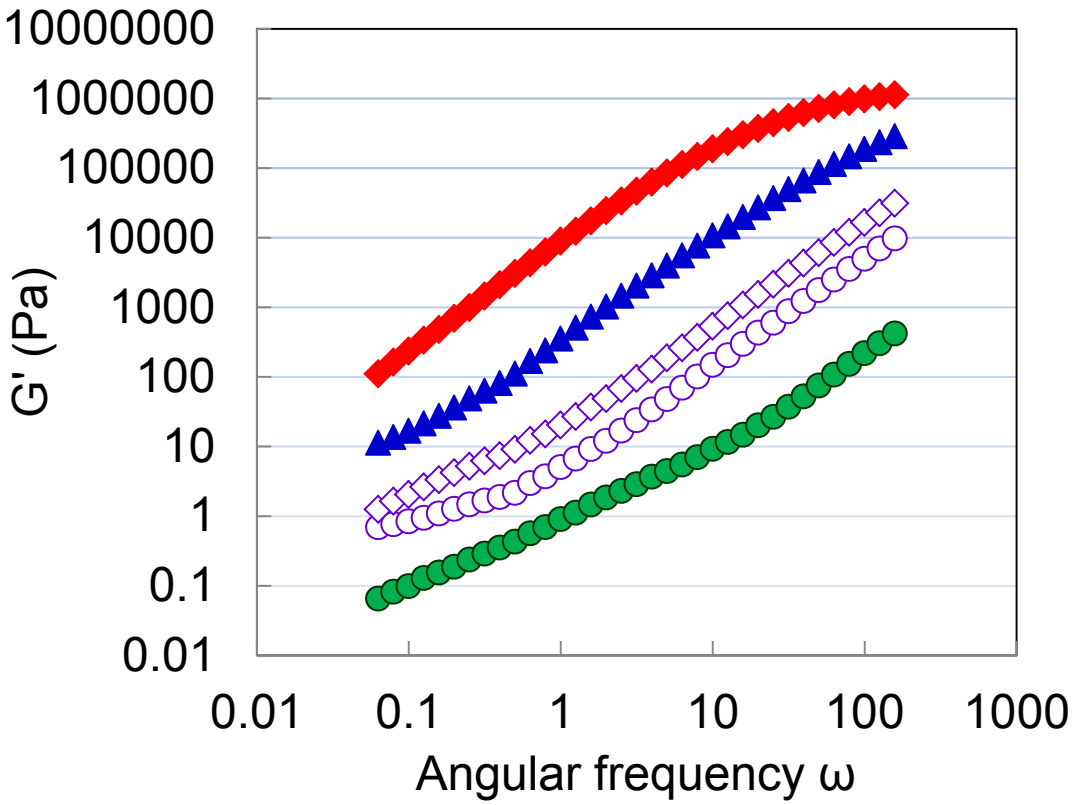

Fig. S1 Storage modulus (G') of F-Lignin-PBD(COOH)$_2$ (◆), W-Lignin-PBD(COOH)$_2$ (▲), A-Lignin-PBD(COOH)$_2$(●), *in situ* 1 (○), and *in situ* 2 (◇), obtained from melt rheology

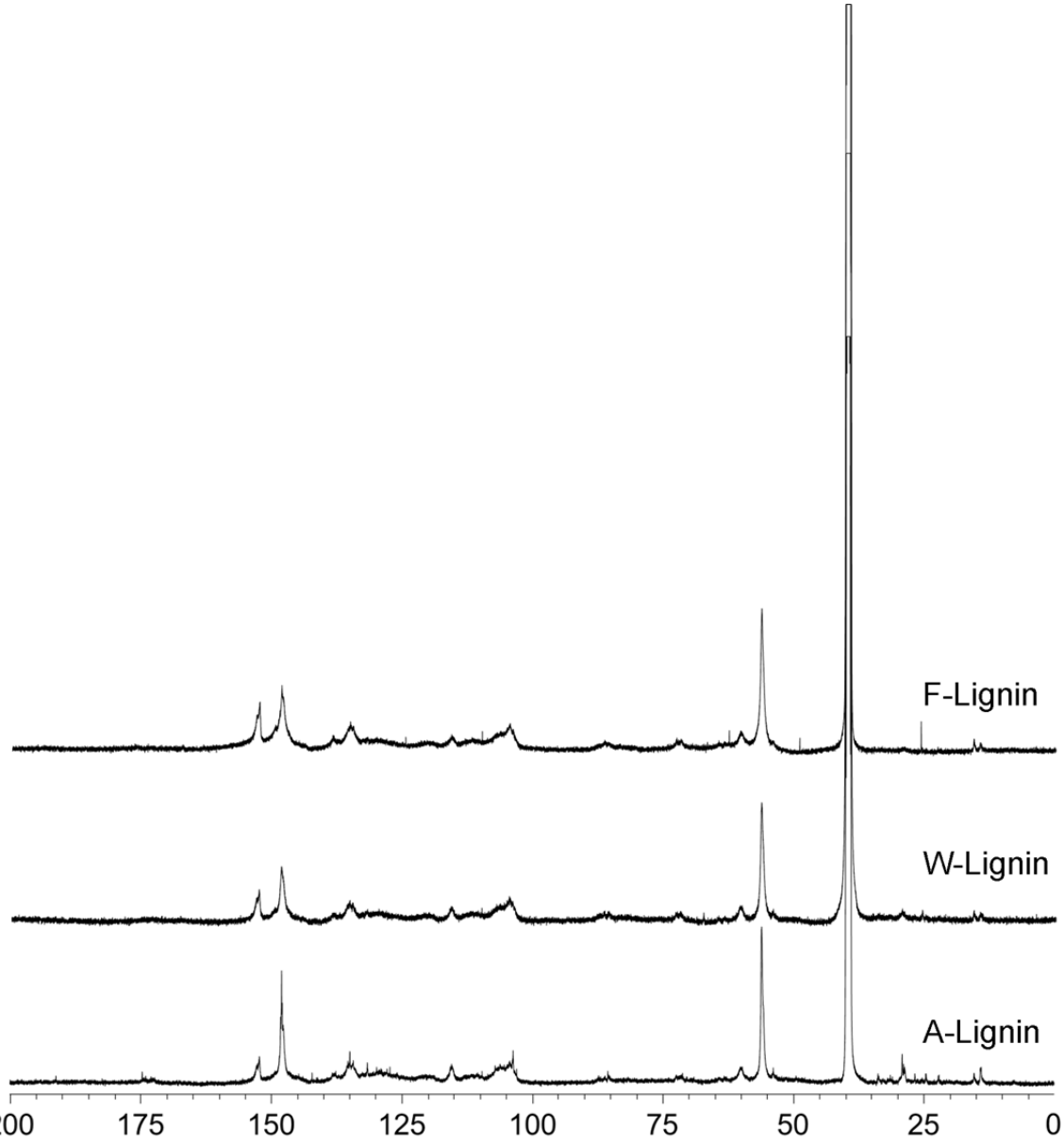

Fig. S2 13C NMR spectra of F-Lignin, W-Lignin and A-Lignin

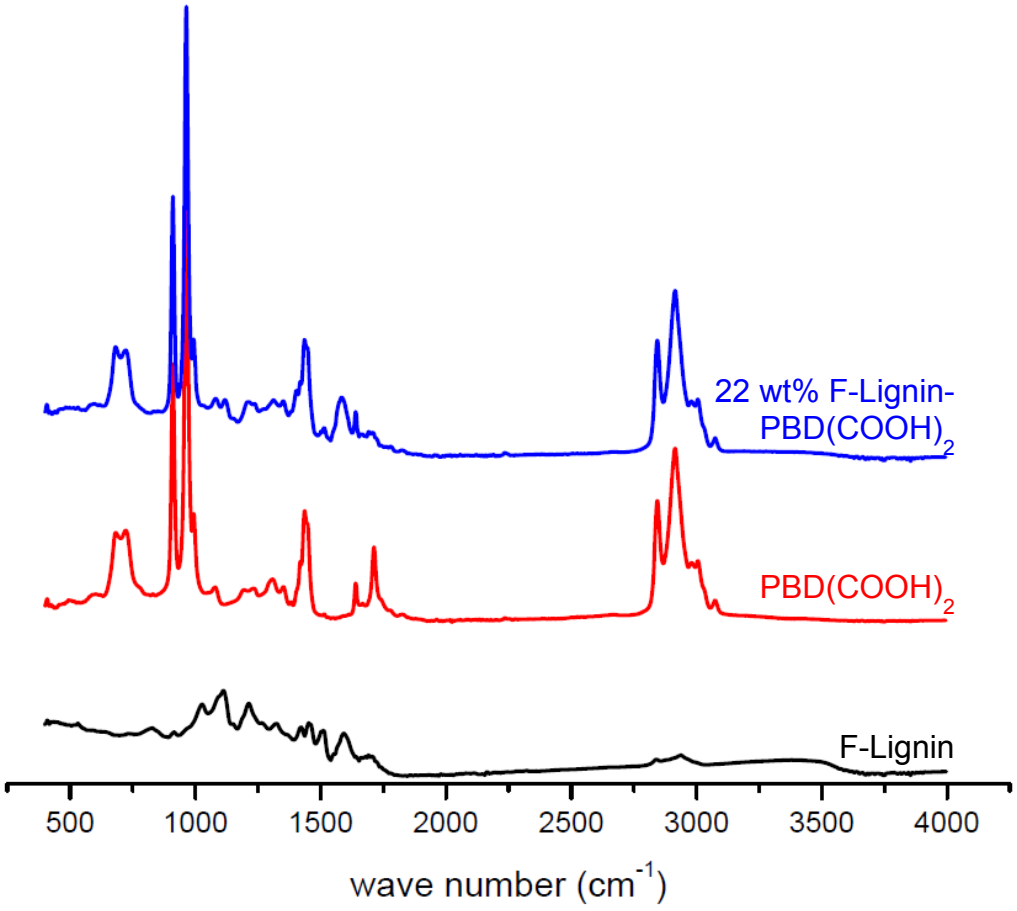

Fig. S3 FTIR spectra of 22 wt% F-Lignin-$PBD(COOH)_2$, $PBD(COOH)_2$, and F-Lignin