

# Step-reaction vs. chain-reaction polymerization of lignin: two facile approaches towards lignin aerogels and carbon aerogels

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Following our previous works on hydro- and aerogels from different lignins cross-linked with oligo(alkylene glycol)- $\alpha,\omega$ -diglycidyl ethers (Passauer et al. 2011a and 2011b; Perez-Cantu et al. 2014) and on the preparation of phenol-formaldehyde (PF) adhesives of high lignin content (Ghorbani et al. 2016), this paper reports the preparation of mechanically stable, monolithic aerogels from ligneous precursor materials that have been brought to gel formation by either step-reaction or chain reaction polymerization. Thermo-induced gelation of ligneous resole resin pre-condensates (40% replacement of phenol by lignin,  $\nu \approx 1000$  mPa·s) in ethylene glycol afforded freestanding, homogeneous gels that were converted to respective aerogels by consecutive neutralization, washing, incremental replacement of water by ethanol and scCO<sub>2</sub> drying. Depending on the extent of resole dilution by ethylene glycol the brownish aerogels featured bulk densities of 40 to 690 mg cm<sup>-3</sup>. Scanning electron microscopy, nitrogen sorption at 77 K and thermoporosimetry using *o*-xylene as probe solvent revealed a largely homogenous internal mesoporous morphology featuring accessible specific surface areas as high as 448 m<sup>2</sup> g<sup>-1</sup>.

In an attempt to increase the lignin content of respective aerogels, different types of lignins were pre-activated by increasing their amount of hydroxyl groups, subsequently permethacrylated and then subjected to radical homopolymerization or copolymerization with methyl methacrylate (MMA) in toluene using azobis(isobutyro)nitrile (AIBN) as radical starter. While copolymerization affords homogeneous gels but inhomogeneous aerogels due to “ballooning effects” during scCO<sub>2</sub> drying of hitherto unknown reason, homopolymerization gives access to both homogeneous gels and aerogels whose shape and dimension can be preserved throughout gelation and scCO<sub>2</sub> extraction of toluene. Preliminary carbonization tests revealed that both types of synthesized ligneous aerogels can be converted to respective carbon aerogels at virtual full preservation of their geometry independent on whether they were first subjected to oxidative stabilization (0.5°C min<sup>-1</sup>, T<sub>max</sub> 250°C, synthetic air) or directly carbonized in argon atmosphere (T<sub>max</sub> 1300°C).

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