

Modeling the Synthesis and Application of Polymeric Catalysts

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ABSTRACT

This study employs two modeling approaches to quantitatively evaluate the influence of crosslink density on the catalytic efficiency of sulfonated styrene-divinylbenzene (DVB) resins. Initially, a styrene-DVB copolymerization model, implemented in Scilab®, introduces the concept of sequences between crosslinks (SBC), denoted as L_E . The SBC length distribution characterizes the degree of crosslinking, and this information was used for the simulation of catalyzed reactions. Figure 1 illustrates the concept of sequences within the polymer support.

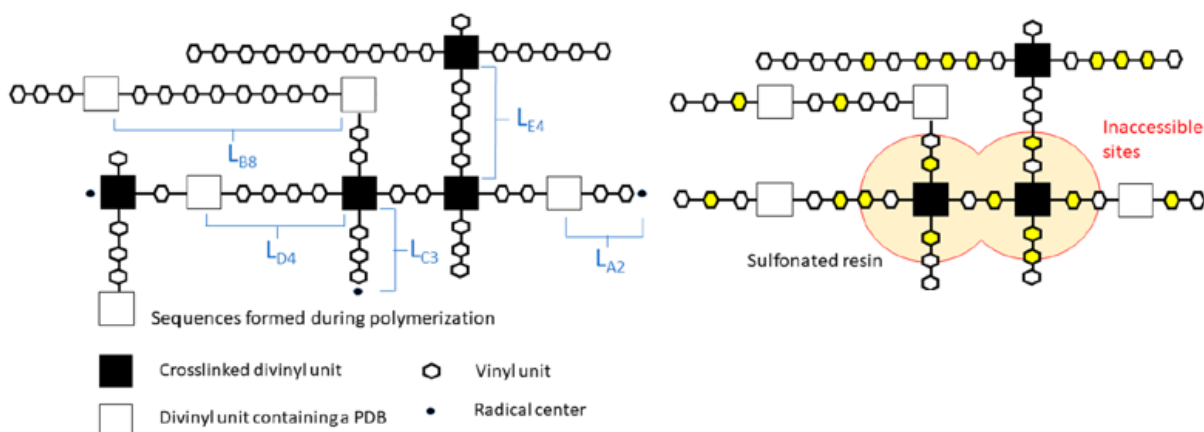


Figure 1 – Pictorial representation of sequences with n vinyl units connecting: a pendant double bond (PDB) to a radical center (L_{An}), two PDBs (L_{Bn}), a cross-linked unit to a radical center (L_{Cn}), a cross-linked unit to a PDB (L_{Dn}) and two cross-linked units (L_{En}). Maximum length considered: $n_{\max} = 100$ units.¹

A second-order pseudo-homogeneous rate equation was applied to esterification reactions catalyzed by acidic resins. The model incorporates a fraction of inaccessible sulfonated units (Y_{ISU}), representing sites inaccessible for catalysis. The study reveals Y_{ISU} ranging from 7% to 72% for resins with 4% and 20% DVB, respectively. This approach provided that the sites contained in SBCs with 6 or less monomer units are inaccessible for the catalyzed reactions studied herein. A linear correlation between the fraction of inaccessible sites and the fraction of short sequences among SBCs was proposed and validated (Figure 2a).

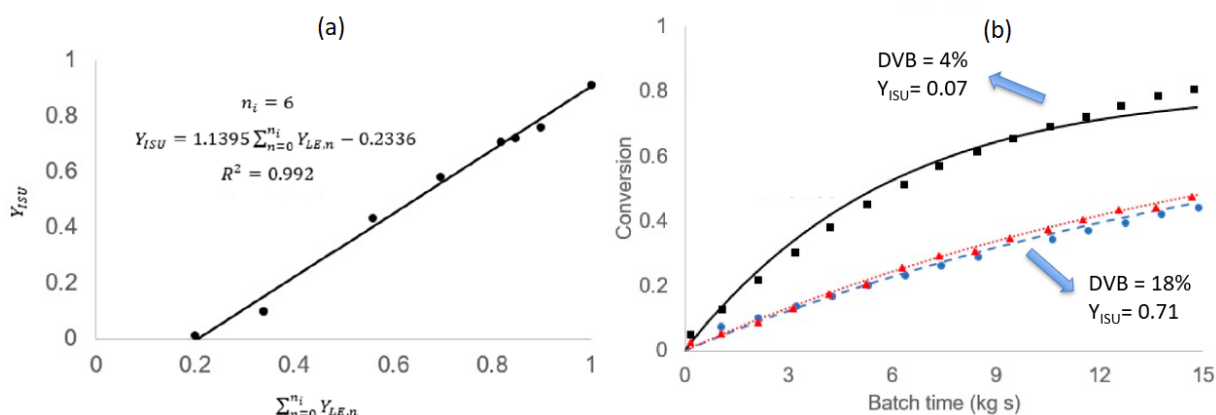


Figure 2 – (a) Correlation between the fraction of inaccessible sites and the sum of fractions of short sequences.¹ (b) Model fitting for the ethyl acetate esterification: Resin concentration= 8.16 g/L, Ion Exchange Capacity \approx 5 mmol/g, alcohol/acido molar ratio = 10 and Temperature = 333 K.²

Figure 2b showcases model fitting for three esterification experiments under similar conditions, except for the catalyst type. The model was validated with data from over 50 experiments in the literature (average $R^2 > 0.9$), conducted with diverse commercial resins. Each point in Figure 2a represents an average of Y_{ISU} values fitted for resins with the same DVB percentages.

This study concludes that the crosslinker content (DVB) significantly impacts the catalytic performance of sulfonated resins. The model provides an initial estimation of the fraction of inaccessible sites, with potential refinement by considering factors such as the size of reacting molecules, textural properties of resins, among others.

References

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- (2) Van de Steene E, De Clercq J, Thybaut, JW. Ion-Exchange Resin Catalyzed Transesterification of Ethyl Acetate with Methanol: Gel versus Macroporous Resins. Chem. Eng. J. 2014, 242, 170–179.