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Application of acidic resins with new formulations as catalysts in solketal synthesis

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Mathematical Modeling

**1. Compolymerization model**

Assumptions

* The sequences distributions are considered to be the same in soluble and gel polymer (gelation was not modeled);
* The distribution of sequences containing only styrene units connecting the extreme groups (LAn to LEn) is considered to be the same as the distribution containing styrene and / or DVB units;
* Only mono-radicals were considered;
* Terminal model.
  1. Balance of species

Table 1 - Copolymerization steps

|  |  |  |
| --- | --- | --- |
| Reaction | Chemical equation |  |
| Initiator decomposition |  |  |
| Styrene Initiation |  |  |
| Divinylbenzene initiation |  |  |
| PDB initiation |  |  |
| Styrene propagation |  |  |
| Divinylbenzene propagation | + PDB |  |
| PDB propagation |  |  |
| Termination |  |  |

: Initiator, : Primary radical, : Monomer of type j, : Polymeric radical, : Pendent double bond, P: Dead polymer, to : Rate constants of the reactions.

(1)

(2)

(3)

(4)

(5)

(6)

In order to estimate the content of soluble chains occluded in the polymer network, balances for linear chain were carried out as follows.

(7)

(8)

(9)

The fraction of occluded soluble chains can be estimated through equation 10.

(10)

Where is the concentration of linear radicals and and are the concentrations of linear and total polymer chains.

* 1. Balance of sequences

Table 2 - Reactions in terms of sequences

|  |  |  |
| --- | --- | --- |
| Chemical equations | | |
|  |  |  |
|  |  |  |
|  | + |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |

: Primary radical, : Vinyl monomer (Styrene), : Divinyl monomer (Divinylbenzene – DVB), : Polymeric radical containing only styrene units, : Dead Polymer, : Polymer fragment, to : Sequences containing *r* repeating units, : cyclic chain containing r units.

(11)

(12)

(13)

(14)

(15)

(16)

(17)

(18)

(19)

(20)

(21)

Equations 1-9 and 11-21 were numerically integrated in Scilab through the algorithm ode. The concentration of crosslinked units, ; total units,; styrene units, ; and DVB units, are equated in (22), (23), (24) and (25) respectively.

(22)

(23)

(24)

(25)

The fraction of crosslinked units and the molecular weight between crosslinks are defined in equations 26 and 27.

(26)

(27)

The swelling index of the simulated polymer network in a given medium was estimated through the algorithm of Karam and Tien (1985) , and the referred equations are shown in 28-31.

(28)

(29)

(30)

(31)

The system was fed with the experimental value of and , provided by the copolymerization model and (dissolved polymer in the supernate was neglected). The system of non-linear equations 28-31 with four unknowns (, , and ) was solved through the function fsolve in scilab. This approach was useful to estimate the particle porosity during the catalytic synthesis of solketal.

and the parameters , , , , and , which are related in the results and discussion section. Occluded phase was neglected in the calculations ( g and g were considered). The four equations and four unknowns: , , and were solved through literature algorithm. 1