Modeling the Effect of Crosslink Density on Resins Catalytic Activities

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ABSTRACT

Two mathematical models were coupled to quantitatively assess the effect of crosslink density on the catalytic activity of sulfonated styrene-DVB resins: (I) a copolymerization model comprising the mass balances of species and sequences, which is used to quantify inaccessible catalytic sites; and (II) a second-order pseudo-homogeneous kinetic model to describe the catalyzed reactions. The fraction of inaccessible sites ranged from 10% to 72% of the total sites for resins with 4% and 20% DVB, respectively. It was found that chain segments with 6 or less monomer units between crosslinks contains inaccessible sites for the catalyzed reactions studied herein. The mathematical approach was validated with 53 catalysis experiments from literature and providing good agreements. A linear correlation for the fraction of inaccessible sites as function of sequences distribution was proposed and validated, providing R² = 0.992. These results can represent a valuable tool to improve the performance of styrene-DVB based catalysts.

**1. Introduction**

Ion exchange resins have been applied as catalysts in different organic reactions over the last decades. Most of these resins consist of a polymer network containing divinylbenzene (DVB) as crosslinker, styrene as the vinyl monomer. What gives the ion exchange character to the resin is the sulfonic groups attached to the styrene aromatic rings. Playing a catalytic role in many reactions, sulfonated Styrene-DVB resins from commercial lines such as Amberlyst® 1, Amberlite® 2, Purolite® 3,4, Dowex® 5, Lewatit® 6, among others, have been extensively studied. Recently, modified resins composed of styrene crosslinked with alternative divinyl monomers such as Ethylene Glycol Dimethacrylate (EGDMA) and Triethylene Glycol Dimethacrylate (TEGDMA) have been synthesized and tested in esterification reactions.7–9 These resins presented promising catalytic activity, indicating that the properties of the polymer matrix and the consequent accessibility to catalytic sites should be better explored. The catalytic efficiency of sulfonated resins depends not only on their porosity, specific surface and ion exchange capacity, but also depends on their degree of crosslinking and consequent swelling indexes. Historically, some attempts to correlate the resin’s degree of crosslinking with its efficiency in catalysis have been conducted by different approaches such as: synthesis and application of resins with different textural properties 10, experimental study of commercial ion exchange resins differed markedly in their polymer structure 11, and development of an empirical equation which takes into account the contribution of each individual fraction of swollen polymer to the overall rate of catalyzed reactions 4. Conversely, a phenomenological approach involving a mathematical characterization of the polymer network and the use of this information in the catalytic process constitute a novelty. One can assert that the matrix properties are a result of the polymerization conditions such as temperature, dilution degree, crosslinker content, among others. Modeling approaches for copolymerization can provide a description of the resin formation and its characteristics at a molecular level.12–14 Information such molecular weight between crosslinks and entrapped pendant double bounds can be estimated by this kind of mathematical model.15

The present study proposes a modeling approach to quantify inaccessible catalytic sites in acidic resins as function of their polymer network structure, and to assess this accessibility effect on catalyzed reactions (mostly esterifications). For this purpose, two specific objectives were defined: (I) to simulate the resin production through a copolymerization model in order to obtain information about the resin structure; (II) to collect the main data, from the copolymerization model, concerning the accessibility through the matrix and use this data in the modeling of resin-catalyzed reactions.

**2. Modeling**

The mathematical approach developed in the present study aims to establish a connection between resin production model and resin-catalyzed reaction model. All the symbols used in their description are defined in the symbology section.

*2.1. Copolymerization model*

The mathematical model conceived herein consists in the description of a vinyl / divinyl free-radical copolymerization. Since most of sulfonated resins are made of styrene crosslinked with divinylbenzene (DVB), this copolymerization system, initiated with benzoyl peroxide (BPO), was considered in the present work. Table 1 relates the copolymerization steps used in the system description.15

Table 1 - Copolymerization steps

|  |  |  |
| --- | --- | --- |
| Reaction | Chemical equation |  |
| Initiator decomposition |  |  |
| Initiation |  | j=1,2 |
| PDB initiation |  |  |
| Monomer propagation |  | j=1,2 |
| PDB propagation |  |  |
| Termination by combination |  |  |

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

The polymeric radical represents the group of all possible polymer radicals in the media (from styrene, DVB and PDB). It is well-known that different radicals have different reactivities. Nonetheless, these reactivities were taken into account in the model by calculating average rate constants, as described in Results and Discussion section.

Sulfonated Styrene-DVB resins from commercial lines such as Amberlyst and Dowex present sulfonic groups (SO3H) which are functional in applications such as ion exchange and catalysis. The ion exchange capacity (IEC) of a sulfonated resin is defined as the mmol (or meq) of SO3H per gram of resin. When this material is applied as a catalyst, the IEC can be understood as the content of catalytic sites. There are several types of sulfonated resins with different crosslinking densities due to the variety of DVB percentage in their composition16, i.e., the greater the DVB content the greater the crosslinking degree. In this sense, when analyzing the effect of crosslinking density on the catalytic activity of the resins, it is expected a higher hindering effect (inaccessible catalytic sites) in resins with higher DVB percentage. The present model describes an attempt to identify regions in the polymer network which are likely to be inaccessible when conducting a reaction catalyzed by a given resin. It is proposed that these inaccessible regions occur around two crosslinked units connected by a sequence of *n* repeating units, this sequence was named LEn. It is understood that smaller LEn sequences can cause higher number of entanglements due to the proximity of the chains. Then, a maximum number of repeating units, ni, was defined as a condition for inaccessibility, i.e., hindering effect occurs in LEn only for n ≤ ni. This approach provides a correlation between the crosslinking degree of the resin and the possible inaccessible sites. In order to model the sequences formation in the resin, the copolymerization kinetics was studied in terms of sequences, as defined in Figure 1.



Figure 1 – Sequences definition and hindering effect.

Figure 1 also illustrates the inaccessible regions considered due to the proximity of two crosslinked units. It is understood that the inaccessibility of a molecule to a given region in the polymer matrix depends on the size of this molecule. In general, sulfonating agents are small molecules 17 which can access more sites than molecules involved in a catalyzed reaction (e.g., esterification). Hence, it was considered that sulfonated units are equally distributed along the polymer matrix regardless of the entanglement degree.

The copolymerization reactions in terms of sequences are presented in Table 2 (subindexes *r* and *s* represent repeating units, same as *n* in Figure 1).

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.

The assumptions considered in the copolymerization model are:

* The sequences distributions are considered to be the same in soluble and gel polymer (gelation was not modeled);
* Cyclization reactions were neglected;
* 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;
* Terminal model.

Concerning the aforementioned assumptions, it is important to point out that, under the studied DVB feedings, the gelation is supposed to occur at the very beginning of the reaction (in general before the first hour)18, i.e., the soluble fraction is very small during most of the reaction period. Additionally, the reactivity of soluble radicals can be considered the same as the reactivity of radical centers along the gel, without impairing the model predictability. Specifically about the modeling of cyclization kinetics, it can be done at cost of considerable computational effort. However, the effect of considering cyclization in the model, for DVB fed in the range 4 - 100 %, is a small shift in monomer conversion and PDBs concentration profiles 19, justifying the neglect of this reaction step. Furthermore, only sequences involving DVB / PDB units were assessed, since they participate in the crosslinking points. Sequences which do not account for the crosslinking density (e.g., sequences connecting two radical centers) were not assessed. Diffusion effects in the copolymerization were neglected due to the degree of dilution studied (150%).

The balances in terms of species and sequences are written as follows.

*2.2. Balance of species*

(1)

(2)

(3)

(4)

(5)

(6)

*2.3. Balance of sequences*

(7)

(8)

(9)

(10)

(11)

(12)

(13)

(14)

(15)

(16)

(17)

Equations 1-17 were numerically integrated in Scilab through the algorithm ode. The concentration of crosslinked units, ; total units,; styrene units, ; and DVB units, are equated in (18), (19), (20) and (21) respectively.

(18)

(19)

(20)

(21)

*2.4. Accessibility to catalytic sites*

The fraction of inaccessible catalytic sites, , was used to calculate the effective ion exchange capacity , i.e., the content of catalytic sites that are available for catalysis (eq. 22).

(22)

The term IEC in equation 22 is a property of the resin which can be collected from the resin supplier or in literature studies (see Results and Discussion section).

It was assumed that the fraction of inaccessible sulfonated units relatively to all sulfonated units is equal to the fraction of inaccessible total units relatively to all units (eq. 23).

(23)

The fraction of crosslinked units is defined in equation 24.

(24)

The fraction of LE,n sequences (containing n units) relatively to all LE sequences is described in equation 26.

(25)

*2.5. Crosslink density*

In the present work, it was adopted the definition from Karam and Tien (1985) 20 for the crosslink density, which is represented by the molecular weight between crosslinks. In the model developed herein, the average molecular weight between crosslinks was estimated by equation 26.

(26)

where:

(27)

The obtained from experimental data was calculated through the following non-linear system of equations. 20

(28)

(29)

(30)

(31)

The system was fed with the experimental value of , , 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. 20

*2.6. Model for catalytic reaction*

Reversible resin-catalyzed reactions in the form were studied, where the limiting reagent was represented by A. The assumptions considered in the catalysis model were:

* Pseudo-homogeneous (PH) approach;
* Ideal mixture;
* The equilibrium conversion was considered to be the highest conversion value obtained for the reaction studied (in general, the last conversion dots constitute a plateau);
* Catalytic sites are equally distributed through the resin particles;
* Non-catalyzed reaction rates were neglected.

Most of the catalyzed reactions studied herein are esterifications, where the reagents (A and B) are alcohol and acid, and the products (C and D) are ester and water.

The following set of equations was written for this part of the model:

(32)

(33)

(34)

(35)

(36)

(37)

(for i= B, C, D) (38)

Considering equations 32-38, on can assert that this model can be applied to reversible resin-catalyzed reactions, and any degree of irreversibility would be tolerable (e.g., ).

In the case of mass transfer limitations, obtaining reaction rates requires more detailed treatment as shown elsewhere. 21

The equilibrium constant () was calculated based on the equilibrium conversion (third assumption). This simplified catalysis model was adopted in order assess the effect of crosslink density on the accessibility of catalytic sites, avoiding complexities such as adsorption / desorption steps. The rate constant k from equation 33 refers to the reaction catalyzed by SO3H, regardless of the type of resin which contains this group. Additionally, the accessibility reduction due to the polymer network characteristics of a given resin is taken into account in the term .

**3. Results and Discussion**

Preliminary simulations were carried out with the copolymerization model in order to identify the value of (number of monomeric units in the longest sequence considered in the model) and assess crosslink density predictions. Table 3 shows the kinetic parameters used in the simulations.

Table 3 – Copolymerization kinetic parameters.

|  |  |
| --- | --- |
| Rate constant | Unit |
| ; |  |
|  |  |
| ; |  |
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| ; |  |
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|  |  |

Data collected from 15

Since the procedures to produce commercial resins is a classified information, a study which reports the synthesis of sulfonated resins with different DVB contents was chosen as base for the copolymerization simulation.22 In the aforementioned study, sulfonated resins with similar features in relation to commercial resins were conceived. Then, the conditions reported in the referred work (1% Benzoyl peroxide, 150% dilution and 90 °C for 30 h) were used in the copolymerization simulations of the present study.

Simulations with different values of were conducted in order to find a range where becomes constant. Figure 2 shows these simulations for n= 0 and n= 9.

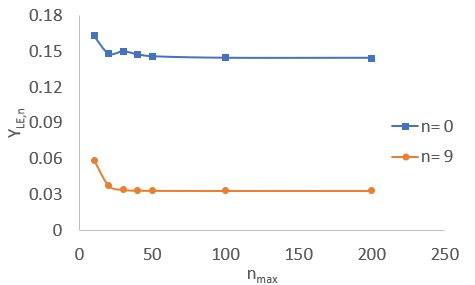


Figure 2 – Determination of the number of monomeric units in the longest sequence to be considered in the model (). Simulation conducted for 10 % DVB.

It can be observed that there is not a considerable difference in for and . Thus, it was adopted for all simulations.

Figure 3 shows a comparison between the estimated in the model and calculated from literature SI data (swelling experiments in toluene).22

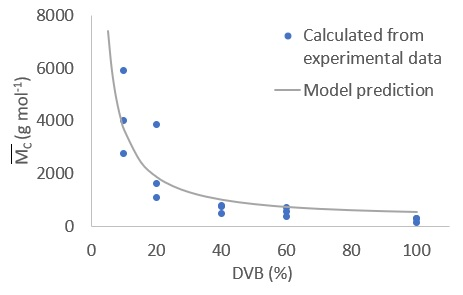


Figure 3 – Crosslink density predictions (from eq. 26). , , , , and . 20,23–27

An acceptable fitting is observed in Figure 3, indicating that the copolymerization model simulated with literature parameters (Table 3) constitute a reasonable approach to represent the crosslinking degree of styrene-DVB resins.

Data from 14 studies on catalysis involving several sulfonated styrene-DVB resins were collected. Studies involving reaction characteristics that are far from the domain of this work, such as oil esterification (multiple reactions) and the use of surface sulfonated resins (e.g., Amberlyst 46), were not included in the analysis. Tables S1 and S2 present the resins properties and the catalyzed reaction conditions respectively.

After applying the second-order PH model to the reaction conditions reported in Table S2, the results shown in Figures S1 and S2 are achieved. In these simulations, the fitting parameters were the fraction of inaccessible sulfonated units () and the rate constant of each reaction catalyzed by SO3H (), both reported in Table S2. Good agreements between experimental data and model predictions can be observed in the aforementioned figures. Nonetheless, the values fitted in the present work were higher than those fitted in literature studies for the same reaction and conditions. This is an expected result, since the constant found in this study represent the effective rate constant of SO3H-catalyzed reaction, while the constant calculated in most literatures is underestimated due to the hindering effect in the resin. It can be cited the following average values obtained for resin-catalyzed reactions from literature: 9.5x10-5 34, 3.4x10-5 41, 1.2x10-4 38 and 4.9x10-5 48; and the respective SO3H-catalyzed rate constants obtained in this work (Table S2): 1.1x10-4, 5.0x10-5, 4.0x10-4 and 9.0x10-5 (all in L2 mol-2 s).

The fitted values are consistent with the resin’s degree of crosslinking, i.e., higher values were found for resins with higher degrees of crosslinking.

It can be stated that depends not only on the crosslinking degree of the resin but also depends on the molecular size of the compounds involved in the catalyzed reaction. However, as an average approach, a mean was calculated for each resin by using information from Table S2. Despite the effect of other process variables on , a correlation of this parameter with DVB percentage could be verified and it is depicted in Figure 4.

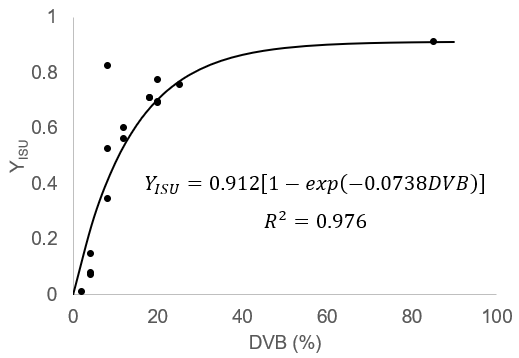


Figure 4 – Correlation between and DVB content in the resins.

The outlier observed in Figure 4 () refers to the resin Amberlite IR120. In spite of the relatively low DVB content (8%), this resin presents the lowest volume of pores among the resins related in Table S1 (VPores = 0.011 cm3 g-1). The higher average obtained for this resin can be attributed to the additional hindering effect caused by its low porosity. Hence, the exponential fit (with R²= 0.976) was adjusted disregarding the dot referred to AIR120.

From the copolymerization model, higher fractions are obtained for higher DVB contents in the range of small values of n (0 – 10), as expected (Figure 5). One can assert that the hindering effect will be more significant around crosslinked units connected by smaller numbers of units. Figure 5 indicates that, working with a given n in the range 0 – 10, it is possible to mathematically represent the effect of crosslink density on the accessibility of catalytic sites in the resin, due to the sharp variations of n in comparison with the behavior observed for higher n values (n > 10).

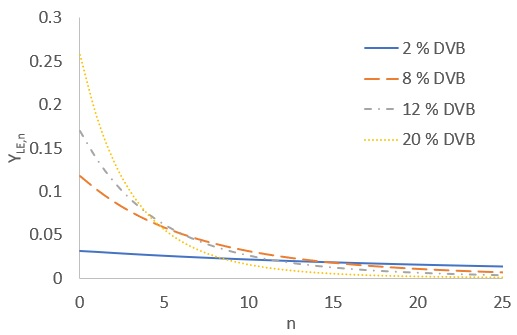


Figure 5 - distribution.

In order to introduce a predictive feature in the present approach, was assumed to be directly proportional to the fraction of inaccessible crosslinked units in the resin, , where is the maximum number of units between crosslinks for occurring hindering effect (i.e., for , does not comprise inaccessible crosslinked units). In other words, the criterion adopted to consider a site inaccessible would be that it is near two crosslinked units connected by or less units, and the fraction of inaccessible sites would have a linear correlation with , as proposed in equation 39.

(39)

The equation 39 was fitted with values of and obtained in the present work. The was determined for each studied DVB percentage. Average values were calculated from Figure 4 for DVB contents of 2, 4, 8, 12, 18, 20, 25 and 85 %. The respective values were calculated firstly for . This fitting procedure was repeated for , , …, , since the range n = 0 – 10 proved to be adequate according to Figure 5. The best fitting result occurred for , which provided R²= 0.992, as shown in Figure 6.

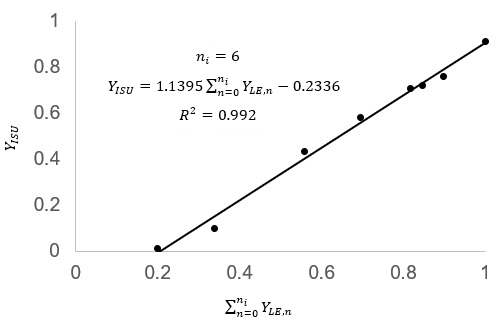


Figure 6 - linear correlation.

As already mentioned, this modeling study is an average approach, since catalytic efficiency do not depend only on the crosslinking degree, but also on system variables such as swelling index, molecular size of reaction components, partition coefficients, among others. Nevertheless, the correlation proposed in equation 39 (determined in Figure 6) is still valid for several literature cases that are close to this linear average behavior, as demonstrated in Figure 7.

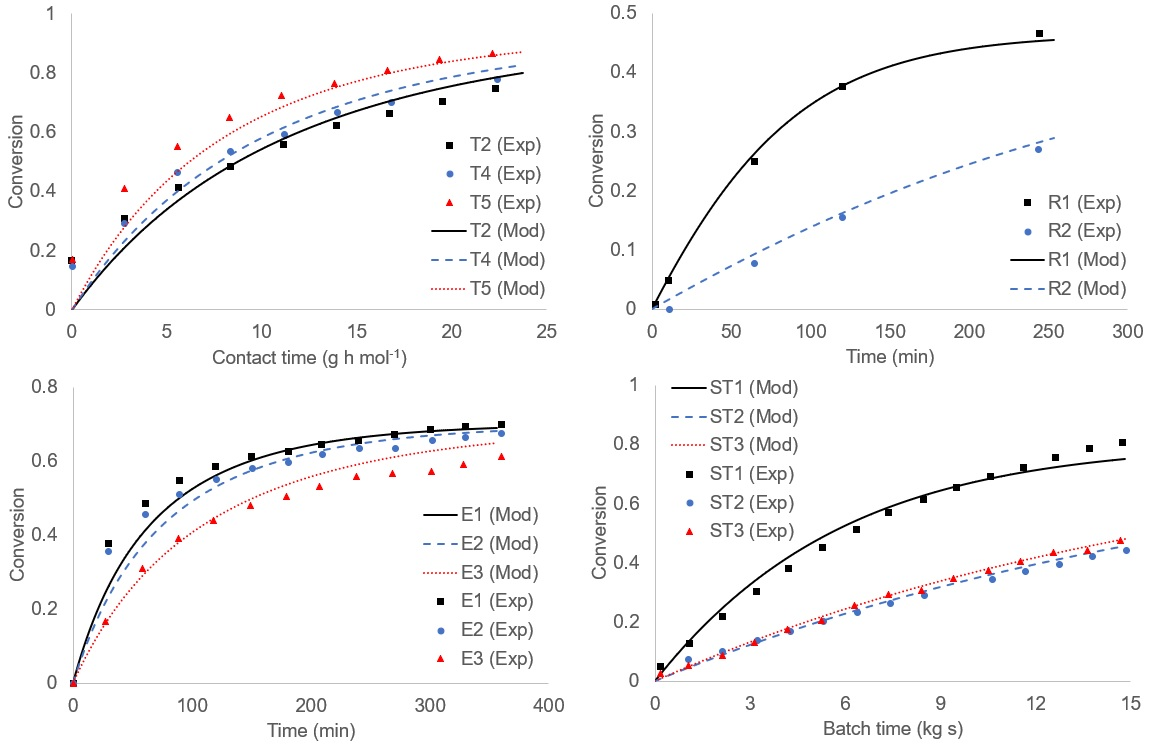


Figure 7 – Fittings obtained with equation 37 (, ) and the same k values from Table S2.

Reasonable fittings are verified in Figure 7, which confirm the applicability of equation 39 in modeling reactions (mostly esterifications) catalyzed by sulfonated resins with many similar characteristics, except for the degree of crosslinking.

The present modeling approach can be refined by validating equation 39 through experiments with less variations: same reaction for all runs and sulfonated resins synthesized under the same conditions, except DVB content (i.e., isolating the effect of crosslinking degree on the catalytic activity).

**4. Conclusion**

A mathematical approach comprising copolymerization and resin-catalyzed reactions was developed and validated with literature data. A maximum of 100 monomer units proved sufficient for the sequences approach applied to the styrene / DVB copolymerization. The copolymerization model was able to represent the trend of crosslink density in function of DVB content, which was confirmed by calculations from swelling index experimental data. The rate constants found for the SO3H-catalyzed reactions are above literature values, demonstrating that the hindering effect can be separated from this parameter. The fraction of inaccessible catalytic sites presented a large range showing values of about 10% (for 4% DVB resins) and 72% (for 20% DVB resins). In average, the fraction of inaccessible sulfonated units followed an exponential profile in function of DVB percentage and a linear correlation with the fraction of inaccessible crosslinks. Based on this linear correlation, it can be concluded that inaccessible crosslinks are connected by, at most, 6 monomer units. This finding is corroborated by the LE,n sequences distribution provided by the copolymerization model, which points out that the main differences between resins with distinct DVB contents occur when considering sequences connected by 0 to 10 monomer units. In summary, the effect of crosslink density on the resin-catalyzed reactions can by quantified through the use of polymerization modeling tools, which provide wealth of information on the polymer network that constitutes the resin.

**Acronyms**

CL Crosslinked unit

DVB Divinylbenzene

F Polymer fragment

IEC Ion exchange capacity

IU Inaccessible units

ISU Inaccessible sulfonated unit

P Dead polymer

PDB Pendant double bond

r.u. Repeating units

SU Sulfonated unit

U Polymerized unit

**Symbology**

|  |  |  |
| --- | --- | --- |
| Symbol | Description | Unit |
|  | Initial concentration of the component a | mol L-1 |
|  | Concentration of the component i | mol L-1 |
|  | Initial concentration of the component i | mol L-1 |
|  | Concentration of HCl solution | mol L-1 |
|  | Reactivity correlation parameter | Dimensionless |
|  | Crosslinked units concentration | mol L-1 |
|  | Initiator efficiency | Dimensionless |
|  | Initiator concentration | mol L-1 |
|  | Ion exchange capacity | meq g-1 |
|  | Effective ion exchange capacity | meq g-1 |
|  | Concentration of inaccessible sulfonated units | mol L-1 |
|  | Concentration of inaccessible units | mol L-1 |
|  | Rate constant of the reaction catalyzed by SO3H | L2 mol-2 min-1 |
|  | Ratio | Dimensionless |
|  | Initiator decomposition constant | s-1 |
|  | Equilibrium constant | Dimensionless |
|  | Styrene initiation constant | L mol-1 s-1 |
|  | DVB initiation constant | L mol-1 s-1 |
|  | Styrene propagation constant | L mol-1 s-1 |
|  | DVB propagation constant | L mol-1 s-1 |
|  | PDB propagation constant | L mol-1 s-1 |
|  | Termination constant | L mol-1 s-1 |
|  | Concentrations of sequences containing r styrene units connecting a PDB to a radical center | mol L-1 |
|  | Concentration of sequences containing r styrene units connecting two PDBs | mol L-1 |
|  | Concentration of sequences containing r styrene units connecting a crosslinked unit to a radical center | mol L-1 |
|  | Concentration of sequences containing r styrene units connecting a PDB to a crosslinked unit | mol L-1 |
|  | Concentration of sequences containing r styrene units connecting two crosslinked units | mol L-1 |
|  | Styrene concentration | mol L-1 |
|  | Initial styrene concentration | mol L-1 |
|  | DVB concentration | mol L-1 |
|  | Initial DVB concentration | mol L-1 |
|  | Average molecular weight between CLs | g mol-1 |
|  | Average molecular weight of polymerized units | g mol-1 |
|  | Number of units between CLs | r.u. |
|  | Maximum n considered for inaccessible CLs | r.u. |
|  | Maximum n considered in the copolymerization modeling | r.u. |
|  | Pendant double bonds concentration | mol L-1 |
|  | Total radicals’ concentration | mol L-1 |
|  | Primary radicals’ concentration | mol L-1 |
|  | Rate of consumption of A | mol L-1 min-1 |
|  | Concentration of radicals containing only styrene units | mol L-1 |
|  | Swelling Index | Dimensionless |
|  | Concentration of sulfonated units | mol L-1 |
|  | Concentration of total polymerized units | mol L-1 |
|  | Concentration of Styrene units | mol L-1 |
|  | Concentration of DVB units | mol L-1 |
|  | Volume fraction of dissolved polymer in the supernate | Dimensionless |
|  | Molar volume of solvent | cm³ mol-1 |
|  | Volume fraction of polystyrene in the swollen occluded polystyrene | Dimensionless |
|  | Volume fraction of rubber in the swollen rubber network | Dimensionless |
|  | Mass of dry resin | g |
|  | Weight of occluded polystyrene in the gel | g |
|  | Weight of rubber in the gel | g |
|  | Conversion of A | Dimensionless |
|  | Fraction of crosslinked units | mol CL (mol U)-1 |
|  | Fraction of among all | mol (mol total )-1 |
|  | Fraction of inaccessible sulfonated units | mol ISU (mol SU)-1 |
|  | Feed ratio between excess and limiting reagents | Dimensionless |
|  | Rubber-solvent interaction factor | Dimensionless |
|  | Polystyrene-solvent interaction factor | Dimensionless |
|  | Density of the polystyrene | g cm-3 |
|  | Density of the rubber | g cm-3 |
|  | Density of the solvent | g cm-3 |

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**Supporting Information**

Tables S1 and S2, and Figures S1 and S2 are in Supporting Information. This information is available free of charge via the Internet at <http://pubs.acs.org/>

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