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Synthesis of Sulfonated Poly[Styrene-co-(Trimethylolpropane Triacrylate)] and Application in the Catalysis of Glycerol Acetylation

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The purpose of this study is the synthesis of a sulfonated resin of styrene cross-linked with trimethylolpropane triacrylate (PS-TMPTA) and its application as a catalyst in glycerol acetylation. The process for obtaining the resins is an aqueous suspension copolymerization at 80°C followed by a sulfonation with sulfuric acid at 57.5°C. Resin characterizations are performed regarding characteristics such as ion exchange capacity and swelling index. The ion exchange capacity (IEC) found for PS-TMPTA (4.4 mmol g⁻¹) is lower compared to those of commercial resins, for example, Amberlyst 36 (5.4 mmol g⁻¹). Despite the low IEC (lower number of catalytic sites), PS-TMPTA presents a relatively high swelling index (2.4) and a higher turnover number (TON = 62.3 h⁻¹) in comparison with the resin Amberlyst 36 (TON = 51.1 h⁻¹) in glycerol acetylation at 80°C with excess of acetic acid.

1. Introduction

Sulfonated styrene-based resins play a key role in science and have applications in many areas, since they have the advantage of being reused and therefore meet current environmental needs.^[1–4] Oversulfonated resins swell better in a polar component than conventionally sulfonated resins. In addition to the polar character associated with sulfonic groups, the degree of cross-linking directly affects the swelling ability of such resins.^[5,6] Sulfonated resins with rigid structures and moderate cross-linking degrees lead to a maximization of polar effects, and when applied as catalysts, they can favor the selectivity of a desired product.^[6]

One of the most consolidated fields for the industrial application of sulfonated resins is the heterogeneous catalysis of organic reactions, where commercial sulfonated styrene-codivinylbenzene (PS-DVB) resins, such as Amberlyst, Dowex, Purolite, have been studied over the last decades. In general, the conversions obtained in organic reactions under moderate temperatures (313–353 K) seem to be not so high (about 65%) when

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using commercial resins as catalysts in the range 3–8 wt%. The highest conversion (about 90%), on the other hand, could be obtained only when the catalyst was used in large concentrations (e.g., 15% by weight or more) and at temperatures of at least 363 K, in addition to the long reaction times.^[7–14]

Ekinci et al.^[12] studied glycerol acetylation using Amberlyst 36 and concluded that glycerol conversion not only increases according to the increment of temperature, but also that there is a selectivity of monoacetin of about 66% at 95°C, with 0.5 g of catalyst, an acetic acid/glycerol molar ratio of 6:1, and 245 min of reaction. The authors also mentioned that both the surface area and ion exchange capacity of the catalysts influenced glycerol conversion.

In addition to divinylbenzene, other cross-linkers have been previously studied in the synthesis of sulfonated resins. Sulfonated poly[styrene-co-(ethylene glycol dimethacrylate)] (PS-EGDMA) has already been studied as a catalyst in the esterification of isoamyl alcohol with acetic acid. Silva et al.^[15] studied this reaction and found promising results for the PS-EGDMA resin in comparison with Amberlyst 36. The same system was studied using 3 g L⁻¹ of catalyst with an acetic acid/isoamyl alcohol molar ratio of 2:1 at 80°C, and an alcohol conversion of 87% was achieved in 2 h of reaction.^[16] Resins with ethylene glycol dimethacrylate have a relatively high swelling index, which can favor the accessibility of the catalytic sites.^[15]

The synthesis of poly[styrene-co-(trimethylolpropane triacrylate)] (PS-TMPTA) was studied about a decade ago by Kong et al.,^[17] who conducted a precipitation polymerization using ethanol and an ethanol/water mixture and concluded that the use of water as a co-solvent is indeed very effective to promote the polymerization to high conversion and to obtain uniform microspheres. Es-haghi et al.^[18] investigated the effect of cross-linker functionality on microgel properties and concluded that the trifunctional cross-linker TMPTA can improve thickening properties more than the other cross-linkers studied.

Despite the copolymerization studies involving TMPTA as cross-linker in styrene-based resins, the sulfonation of this material and subsequent application in catalysis of organic reactions were not previously investigated. The present work aims to synthesize sulfonated PS-TMPTA, characterize the resulting material, and test it as a catalyst in glycerol acetylation. ADVANCED SCIENCE NEWS ______ www.advancedsciencenews.com

2. Experimental Section

2.1. Materials

The chemicals and their respective purities and suppliers are described below.

Copolymerization step: benzoyl peroxide (BPO) 72–80% (Vetec), styrene 99% (Sigma Aldrich), trimethylolpropane triacrylate (TMPTA) 99% (Sigma Aldrich), toluene 99.5% (Isofar), heptane 99% (Synth), polyvinyl alcohol (PVA) 95% (Dinâmica), N₂ (White Martins) and distilled water.

Sulfonation step: sulfuric acid 95-98% (Química Moderna).

- Catalysis step: glycerol 99.5% (Ultra) and acetic acid 99.8% (Ultra).
- Analyses: methanol 100% (Synth), nitric acid 1 mol L^{-1} (Dinâmica), sodium hydroxide 97% (Ultra), phenolphthalein (Sigma Aldrich), hydrochloric acid 0.1 mol L^{-1} (Ultra), and potassium bromide 99% (sigma Aldrich).

All chemicals were used as received.

2.2. Copolymerization

The copolymerization of styrene with TMPTA was carried out in a 1-L jacketed glass reactor at 80°C under mechanical stirring of 350 rpm for 6 h. An aqueous suspension copolymerization was prepared with a volumetric ratio of 0.13 between the organic phase and the aqueous phase and 0.05% (weight) of PVA in the aqueous phase. In the dispersed phase, the following volumetric composition was used: 40% of monomers in the organic mixture and 50% of toluene in the toluene+heptane mixture; and the following molar fractions were used relative to the monomeric mixture: 0.01 of TMPTA and 0.04 of BPO (initiator efficiency f =0.15). After the suspension copolymerization, the particles were filtered, washed with water (200 mL) and methanol (100 mL), and then dried. This formulation and the experimental conditions were based on previous literature studies.^[17,19]

2.3. Sulfonation

The resin obtained from the copolymerization step was submitted to a sulfonation procedure at 57.5°C under a stirring speed of 175 rpm for 1 h. The proportion used in this stage was 1 g of resin for 18 mL of sulfuric acid. After the sulfonation process, the reactor content was slowly diluted in distilled water and the sulfonated particles were separated by filtration. The particles were extensively washed with distilled water in order to remove all the residual sulfuric acid. This washing procedure was concluded when there was no pH variation in the water containing the particles. Details on the sulfonation process can be found elsewhere.^[4]

2.4. Glycerol Acetylation

Glycerol acetylation is a series of reactions where acetates substitute OH groups to form Monoacetin (Equation 1), Diacetin (Equation 2), and Triacetin (Equation 3)^[20] using sulfonated www.ms-journal.de

resins as catalysts, i.e., SO₃H groups as catalytic sites.

$$Glycerol(G) + Acetic Acid(A) \xrightarrow{SO_3H} Monoacetin(M) + Water(W)$$

$$\begin{array}{l} \text{Monoacetin} (M) + \text{Acetic Acid} (A) \xrightarrow{SO_3H} \text{Diacetin} (D) + \text{Water} (W) \\ \rightleftharpoons \end{array}$$

$$\begin{array}{l} \text{Diacetin} \left(D \right) + \text{Acetic Acid} \left(A \right) & \stackrel{SO_3H}{\rightleftharpoons} \text{Triacetin} \left(T \right) + \text{Water} \left(W \right) \\ \end{array}$$

(3)

In addition, the isomers 1-monoacetin and 2-monoacetin can be formed during the process, as well as 1,2-diacetin and 1,3diacetin. In the present study, the isomer amounts were summed and simply called Monoacetin (M) and Diacetin (D).

Glycerol and acetic acid were fed to the reactor in the proportion 1:4 (molar). The reaction was carried out with and without catalyst at 80°C under agitation of 355 rpm for 6 h. The same experimental conditions were set for both the first (R1) and second (R2) use of the catalysts. Aliquots were withdrawn throughout the reaction and the compositions were analyzed through titration and gas chromatography (GC). For comparative purposes, the acetic acid was quantified both by titration with a NaOH solution (1 mol L⁻¹) and phenolphthalein as indicator and also by GC. The conversion was calculated only for glycerol, since it is the limiting reagent. The concentration of each component was quantified by GC (Shimadzu Nexis GC 20-30) using the column SH-Rtx-5 and the following conditions. In the quantification methodology for acetic acid, the injection and column temperatures were 160°C and 30°C, respectively, while the detector operated at 260°C. The analysis ramp for acetic acid began at 30°C ending at 50°C, at a rate of 5°C min⁻¹.^[21] For the quantification of glycerol and its acetates, the injector, column, and detector temperatures were 210°C, 125°C, and 250°C, respectively. The ramp started at 125°C and remained at this temperature for 5 min. It was then raised to 160°C at a rate of 5°C min⁻¹.^[22]

In order to build the calibration curve, reagents with known concentrations (read from the manufacturer's vial) of each reaction medium component (except water) were diluted in methanol in the proportions 3156, 631, 350, and 240 ppm each. The retention times obtained in the chromatographic analysis were correlated with the respective concentrations in the above dilutions, resulting in the calibration curves used in this study.

To quantify the sample compounds, the proportion of 0.02 g of sample/0.008 L of methanol was used in the GC analysis. In the chromatogram shown in **Figure 1**, the peaks of glycerol and glycerol acetates can be seen. The residence times found herein are in agreement with the literature values.^[22]

2.5. Analyses

2.5.1. Ion Exchange Capacity

The following procedure was used for both catalysts (Amberlyst 36 and PS-TMPTA). The amount $W_d = 0.5$ g of dry sulfonated





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Figure 1. Typical chromatogram obtained in the glycerol acetylation.

polymer was added to 8 mL of nitric acid solution (1 mol L⁻¹) and left to stand for 4 h. The particles were then filtered, dried to constant mass, and put in contact with $V_{\text{NaOH}} = 25$ mL of NaOH solution (0.1 mol L⁻¹). After about 16 h, the solution was titrated with HCl solution ($C_{HCl} = 0.1 \text{ mol } L^{-1}$), using phenolphthalein as indicator. The titrated volumes (V_t) were used to calculate the ion exchange capacity (IEC) according to Equation 4.

$$IEC = C_{HCl} \frac{\left(V_{NaOH} - V_{t}\right)}{W_{d}}$$
(4)

2.5.2. Swelling Index

After each catalyzed glycerol acetylation experiment, the resin particles were filtered and their mass (swollen with reaction fluid) was measured (W_{sw}). The particles were then dried until constant mass and their dry weight was measured (W_d). The Swelling index (*Sw*) was calculated as shown in Equation 5.

$$Sw = \frac{W_{sw}}{W_d}$$
(5)

The procedures used in these analyses were based on a previous study. $\ensuremath{^{[4]}}$

2.5.3. Fourier Transfer Infrared (FTIR) Analysis

The FTIR methodology reported in literature^[23,24] was used in the present study: 10–20 mg of the resin sample was mixed with 200 mg (approximately) of potassium bromide (KBr) and then placed in a hydraulic press to form a disc. The spectrometer was operated in the infrared wage range (500–4500 cm⁻¹).

Table 1. Experimental conditions.

Experiment	Catalyst concentration [g L ⁻¹]	Acetic acid/glycerol molar ratio	Temperature [°C]	Reference
Blank	0.0	4.00	80	This study
PS-TMPTA	5.0	4.00	80	This study
A36	5.0	4.00	80	This study
L1-Blank	0.0	3.90	80	[23]
L1-A15	46.7	3.90	80	[23]
L2-A36	2.3	0.13	105	[24]
L2-D2	2.3	0.13	105	[24]

3. Results and Discussion

The catalysis of glycerol acetylation was carried out in the present study by using a synthesized (PS-TMPTA) and a commercial resin (Amberlyst 36). A blank reaction, without catalyst, was also conducted. Literature studies (L1 and L2)^[23,24] on glycerol acetylation were compared with the results obtained here. **Table 1** shows the experimental conditions considered in each reaction.

Glycerol acetylation occurs through the acidic catalysis route; as such, autocatalysis takes place due to the presence of the reagent acetic acid. This reaction without the presence of sulfonated resin produces low conversion in comparison with the catalyzed reaction, as can be seen in **Figure 2**.

A trend close to a plateau can be observed at the end of the reaction (360 min of reaction), reaching about 40% of conversion for the Blank reaction and about 90% of conversion for the A36 and PS-TMPTA experiments. On one hand, the conversions obtained for both catalysts (A36 and PS-TMPTA) become similar as the reaction tends to equilibrium; on the other hand, the higher reaction rate observed for the resin cross-linked with

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Figure 3. Glycerol acetates selectivity.

TMPTA is evident in Figure 2. The faster glycerol consumption in PS-TMPTA experiment relatively to A36 is corroborated by the product formation displayed in **Figure 3**.

At 30 min of reaction, the monoacetin (M) selectivity reaches its maximum value, which is 0.84 for PS-TMPTA and 0.36 for A36. The diacetin (D) selectivities are higher for PS-TMPTA than for A36 in the 90–300 min range. On average, the diacetin selectivity is 21% higher for PS-TMPTA than for A36 in the referred range. It can therefore be stated that under these conditions, PS-TMPTA is the preferred catalysts when high diacetin selectivities are required. Conversely, when monoacetin is the desired product, PS-TMPTA is preferred in processes that reach relatively low reaction extents (e.g., Continuous Stirred-Tank Reactor). As can be seen, low triacetin selectivities were achieved for both catalysts for the conditions under study. Literature studies show low selectivity for triacetin (about 6%) in catalyzed glycerol acetylation, which is a common result for this reaction conducted at relatively mild temperatures, such as 80°C.^[23]

The turnover number (TON) represents a quantification of the efficiency of catalytic sites and can be calculated with Equation 6 according to Boudart.^[25]

$$TON = \frac{Nc}{Cat \cdot t} \tag{6}$$

where:

TON turnover number (h⁻¹) N_C number of mols of acetic acid consumed (mmol)



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Figure 4. Turnover numbers. a) Reactions without catalyst; b) Catalyzed reactions.

Cat number of mols of catalytic sites (mmol) *t* reaction time (h)

In the present work, TON was also calculated for the blank reactions (auto catalyzed by the acetic acid). In these cases, the unreacted acetic acid was considered as catalytic site (Cat in Equation 6).

The TON was first calculated for the reactions without catalyst (Blank and L1-Blank), as shown in **Figure 4**a. In these cases, the TON values were calculated considering the remaining mols of acetic acid at each reaction time as catalytic sites. TON values below 0.14 h^{-1} were obtained for both experiments, revealing the low efficiency of acetic acid as a catalyst for this reaction. It is important to note that the acetic acid concentration changes as the reaction progresses. However, if the initial number of mols of acetic acid (the highest along the reaction) was considered in the TON calculation, the values reported in Figure 4a would be even lower than those calculated with the instantaneous acetic acid amount. Thus, the TON obtained for autocatalysis is negligible when compared with the TON obtained for heterogeneous catalysis, that is, when solid acidic catalysts are used, the TONs are considerably higher, as illustrated in Figure 4b.

As listed in Table 1, the acetic acid/glycerol molar ratio of 3.9 was used in experiment L1-A15 and the molar ratio of 4.0 was used in both the A36 and PS-TMPTA experiments. Since 80°C was set for these three experiments, their conditions are very similar, except for the catalyst loading. Based on the TONs observed in Figure 4b, the catalyst efficiencies can be listed from highest to lowest as follows: PS-TMPTA>A36>L1-A15. It is understood









Figure 6. Glycerol acetylation at 105°C. Comparison of TONs for different resins.

that the more contact there is between reagents and catalytic sites, the higher the reaction rate will be. When sulfonated resins are used as catalysts, the cross-linking density plays an important role in this contact. The cross-linking density is correlated with the resin's swelling ability. In this sense, it is expected that resins with a higher swelling index in the reaction fluid achieve higher TONs. This correlation can be observed for the cases discussed here, as can be seen in **Figure 5**.

Additionally, the cross-linking density depends on the percentage of cross-linker added to the polymer network. Dosuna-Rodriguez et al.^[24] studied the catalysis with different resins at 105°C. The effect of the divinylbenzene percentage on the resin can be observed by calculating the TON for two experiments conducted under the same conditions except for the resin type (L2-A36 and L2-D2). These results are reported in **Figure 6**.

A clear discrepancy can be observed in the first 120 min of reaction, and the same phenomenon is observed in Figures 2, 3, and 4b. These results can be explained by the different contact efficiencies of the fluid/catalytic sites among the resins, as mentioned before, and the solvation time during the reaction process. The latter could be an explanation for the discrepancies observed between the curves in Figure 6, since the resin with the highest cross-linking density, Amberlyst 36 (12% DVB), may present a delay in solvation in comparison with the resin Dowex 50Wx2 (2% DVB). One feature that could enhance the solvation and consequent catalytic efficiency is the affinity between the



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Figure 7. FTIR analysis. a) PS-TMPTA Structure; b) Identification of sulfonic groups in A36 and PS-TMPTA resins. W.S: without sulfonation, V.: virgin resin, R1: after first use in catalysis, R2: after second use in catalysis.

reaction fluid and the resin. The difference between TMPTA and DVB lies in their polarity characteristics. The acrylate groups present in TMPTA may favor the use of PS-TMPTA as a catalyst in glycerol acetylation, since it is a medium containing polar groups in its compounds. **Figure 7** shows the infrared spectra for both resins, PS-TMPTA and Amberlyst 36. In the synthesized resin (PS-TMPTA), the presence of ester groups in the region from 1700 to 1800 cm^{-1[26,27]} related to the stretching of C=O is observed. After the sulfonation step, a significant decrease of this group is observed, which can be attributed to hydrolysis, since water is formed in this process. The peak in the region from 1010–1020 cm⁻¹ confirms the presence of SO₃H groups (catalytic sites of the resins).

The region assigned to symmetric and asymmetric stretching vibration of $SO_3^{[28-30]}$ is shown in Figures 7a and 7b, with Figure 7b presenting a comparison between the structures of the

Table 2. Resin characteristics and average results.

Experiment	Cross-linker	Cross-linker percentage	Swelling index	IEC[mmol g ⁻¹]	TON [h ⁻¹]	Reference
PS-TMPTA	тмрта	1 ^{a)}	2.4	4.4	62.3	This study
A36	DVB	12	1.7	5.4	51.1	This study
L1-A15	DVB	20	1.5	4.7	40.9	[23]
L2-A36	DVB	12	-	5.4	52.5	[24]
L2-D2	DVB	2	-	4.8	90.4	[24]

^{a)} TMPTA fed in the copolymerization step.

Table 3. Ion exchange capacity decay.

Resin	IEC [mmol g ⁻¹]
PS-TMPTA	4.40
PS-TMPTA R1	3.50
PS-TMPTA R2	3.45
A36	5.40
A36 R1	4.75
A36 R2	4.35

R1: after first use of the catalyst; R2: after second use of the catalyst.

resins. These spectra corroborate the ion exchange capacity decay results presented in **Table 3**. **Table 2** summarizes the resin characteristics and the respective results. It is important to emphasize that the ion exchange capacity obtained for PS-TMPTA was 4.4 mmol g⁻¹, while the IEC of Amberlyst 36 was 5.4 mmol g⁻¹, i.e., the number of catalytic sites (sulfonic groups) present in the A36 experiment was higher than in the PS-TMPTA experiment. This is additional evidence that the availability of the sulfonic groups for the catalytic process depends on the capacity of the resin to promote contact between these groups and the reaction medium.

Table 3 reveals a slight decay in ion exchange capacity in comparison with virgin resins (sulfonated but without any use). However, this small reduction in the catalytic sites did not affect the catalysis significantly.

Experiments were carried out to evaluate the catalytic decay from the resins, and the results are shown in **Figure 8**.



Figure 8. Catalytic activity decay. R1: first use in the catalysis; R2: second use in the catalysis.

A small decay in catalytic activity can be observed for PS-TMPTA R2 (second use). A possible explanation for this loss in catalytic activity is the hydrolysis of the ester groups present in TMPTA, and the consequent breaking of chains due to the formation of water in glycerol acetylation. The results provided by PS-TMPTA in its first use were slightly better compared to A36, probably due to the longer TMPTA length in comparison with divinylbenzene (in Amberlyst 36). The longer length and higher swelling index for PS-TMPTA could be contributing to the accessibility of reagents to the catalytic sites of the resin. In further studies, the use of different cross-linkers, such as long chain dienes, could avoid hydrolysis and be promising for the stability of the catalytic activity in the referred reaction.

4. Conclusion

A sulfonated resin made of styrene cross-linked with trimethylolpropane triacrylate was synthesized and tested as a catalyst in glycerol acetylation. In this reaction medium, the synthesized resin achieved a higher swelling index in comparison with commercial sulfonated styrene-co-divinylbenzene resins. This feature can be explained by the polar character of the compounds in the glycerol acetylation medium, which may interact with acrylate groups in TMPTA. Chemical affinity issues and the crosslinking density of the polymer networks in the resins affect their swelling indexes and consequent efficiencies in the catalysis, i.e., more affinity with the reaction medium and less cross-linking density lead to more contact between the reagents and the catalytic sites (sulfonic groups). Glycerol conversions close to the equilibrium conversion could be observed at 6 h of reaction at 80°C and with excess of acetic acid for both catalysts: Amberlyst 36 and PS-TMPTA. Nevertheless, in the first 120 min of acetylation, the reaction rate was clearly higher for the case catalyzed by the PS-TMPTA resin than for the case catalyzed by Amberlyst 36, despite the latter having a higher ion exchange capacity. The same rate difference was observed for the reactions involving the glycerol acetates. The higher reaction rates obtained by PS-TMPTA in the first 120 min of reaction are an advantage when choosing a catalyst to be used in continuous reactors, since the residence time required to obtain such rates would be shorter in comparison with the commercial resin. In conclusion, the chemical characteristics of sulfonated poly[styrene-co-(trimethylolpropane triacrylate)] are favorable to its application as a catalyst in glycerol acetylation.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

catalyst, resin, styrene, sulfonation, TMPTA

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