

Building of a sulfonyl-group-functionalized monomer whose polymer is able to catalyze biodiesel formation

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ABSTRACT: A linear polymer containing sulfonyl groups was synthesized from a vinyl monomer to use its acid group as a catalyst of the esterification of oleic acid to form biodiesel. First, synthesis optimization of the monomer was carried out in an aqueous system. This molecule was obtained in an excellent yield, where the pH and reaction time were decisive factors in the synthesis performance. The vinyl monomer was then polymerized, and the catalytic activity of the sulfonic acid could be demonstrated in the esterification of oleic acid with short-chain alcohols. The increase in the catalyst content resulted in a higher concentration of the carbonyl group activated, and this was followed by faster esterification kinetics. The highest yield (98 mol %) was reached after 20 min when a 10 mol-% of catalyst was used. A larger size alcohol led to slower esterification kinetics because its ability as a nucleophile was decreased by steric impediment. The sulfonyl group in polymer **4**, an aryl sulfonic acid polymer, proved to be an acid almost as efficient as sulfuric acid, although the former worked in a heterogeneous system. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41957.

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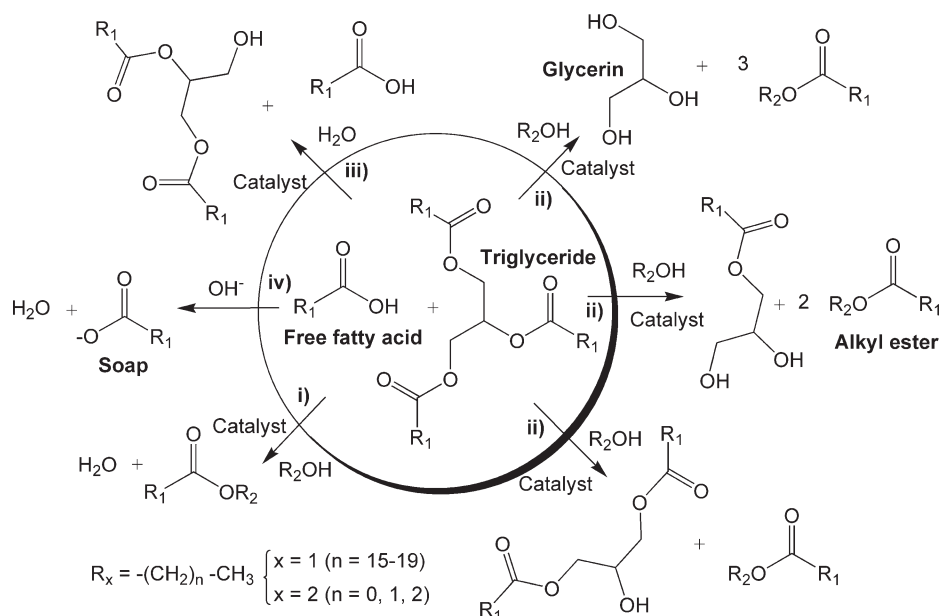
INTRODUCTION

The progressive increase in fuel prices and the demand for global energy have awakened a growing interest in the development of alternative energies from nonpollutants and renewable resources, of which biofuels seem to be the most promising.^{1–3} Among green fuels, it is possible to regard biodiesel as an alternative fuel for diesel engines, whose molecular structure agrees with an alkyl ester.^{4–8} This compound is mainly generated from the reaction between vegetable oil or animal fat and a short-chain alcohol (Scheme 1).⁹ Initially, biodiesel was obtained from either a simple esterification or transesterification reaction catalyzed by an acid or basic compound in a homogeneous system. Although the transesterification of renewable lipids under base catalysis is the industrial process commonly used for biodiesel formation, acid catalysis has clear advantages.¹⁰ It is not affected by the presence of free fatty acids, which produce soap in a basic medium; it also simultaneously promotes esterification and transesterification reactions.^{10,12} Therefore, acid catalysis is a suitable system for generating biodiesel from discarded cooking oils with a high content of free fatty acids.^{13–16} When homogeneous and heterogeneous catalysis are compared, the latter offers rapid product separation and easy catalyst recovery; this contributes to a signifi-

cant decrease in the process time. In addition, the corrosive activity of the heterogeneous catalyst is almost zero, and this reduces the number of washing steps and effluent generation.¹⁷ Although a large number of heterogeneous catalysts have been reported in esterification and transesterification reactions, in the past, some restrictions on the process have limited their use for the practical production of biodiesel.^{18,19} However, a range of new strategies is currently being developed for biodiesel synthesis to enhance the applicability of heterogeneous catalysis, including the use of catalysts attached to supports.^{13,20–23} The building of a new monomer, whose molecular structure is designed to achieve singular requirements for a particular application, is a topic addressed continuously as a challenge in the field of polymeric material synthesis. Moreover, it is known that an increase in the acidity of the organosulfonic acid group significantly improves the catalyst activity for fatty acid esterification reactions.²⁴ Melero *et al.*²⁵ showed that the acid strength of the sulfonic acid group increased when a more electron-withdrawing group (e.g., phenyl group) was incorporated. Therefore, in this article, we present the preparation of a phenyl sulfonic acid functionalized monomer and its polymer. Furthermore, the catalytic ability of the sulfonyl group conjugated to polymer chain was studied for the formation of

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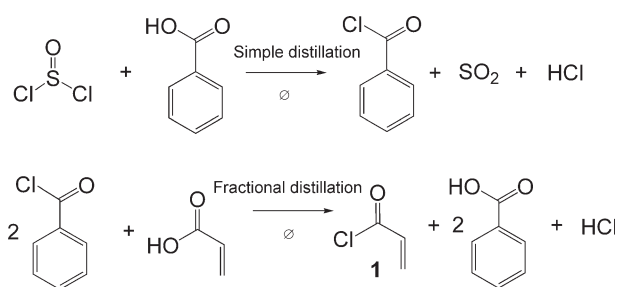
Scheme 1. Formation of biodiesel from vegetable oils or animal fats with different catalysts in the reaction mixture: (i) esterification, (ii) transesterification, (iii) ester hydrolysis, and (iv) saponification reaction.

oleic acid esters in heterogeneous systems (Scheme 1). First, 4-(acryloylamino)benzene sulfonic acid (monomer **3**) was synthesized from the reaction between acryloyl chloride (**1**) and sulfanilic acid (**2**) in an aqueous system (Scheme 2). This monomer was later polymerized in aqueous solution by the addition of a radical initiator, such as ammonium persulfate (Scheme 3). Monomer **3** and its polymer **4**, an aryl sulfonic acid polymer, were characterized by ultraviolet–visible (UV–vis) spectroscopy, Fourier transform infrared (FTIR) spectroscopy, and ^1H - and ^{13}C -NMR spectrometry. The catalytic activity of the solid acid catalyst could then be verified for oleic acid esterification with primary alcohols. The content of sulfonyl groups and alcohols with different chain lengths and the reaction temperature were the esterification variables from which some kinetic parameters could be calculated to propose a kinetic model.

EXPERIMENTAL

Reagents and Equipment

The description of the reagents used for the development of this study is provided as follows. Acrylic acid (AAc; pro analysis (p.a.), Merck, Germany) was purified by distillation under reduced pressure. Thionyl chloride (SOCl_2 ; p.a., Riedel de

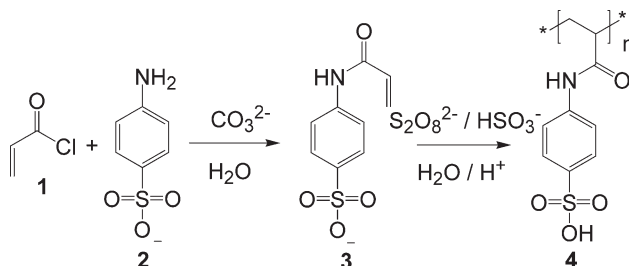


Scheme 2. Formation of **1** with reactive distillation between benzoyl chloride and AAc.

Hagen, Germany) was purified by simple distillation. We also used the following: sulphanic acid (**2**) (p.a., Merck, Germany), ammonium persulfate (p.a., Ciccareli, Argentina), hydroquinone (p.a., Riedel de Hagen, Germany), oleic acid (p.a., Anedra, Argentina), methanol (p.a., bp = 65°C, Ciccareli, Argentina), ethanol (96 vol %, bp = 78°C, Porta, Argentina), 1-propanol (p.a., bp = 97°C, Ciccareli, Argentina), sulfuric acid (98 wt %, Merck, Germany), and Permutit Q (a commercial cation-exchange resin, Permutit Co., Inc.). Sodium sulfonate functionalized resin was exchanged to its acid form by the addition of an excess of a 3M HCl solution; the supernatant was eliminated and dried the resin *in vacuo* until a constant mass was reached. Spectrophotometric measurements were recorded on a MultiSpec-1501 Shimadzu spectrophotometer (Japan). FTIR spectra were carried out on a Nicolet 5-SXC spectrometer. ^1H -NMR spectra of the liquid samples were recorded on a Bruker 400 spectrometer (Germany).

Synthesis of **1**

In a round-bottomed flask connected to an overhead reflux condenser, a molar ratio of 4 : 1 of thionyl chloride (250 mL) to benzoic acid (100 g) was added and boiled for 30 min (Scheme 2). Pure benzoyl chloride was then obtained by simple



Scheme 3. Synthesis of the vinyl monomer and its polymer in respective aqueous reaction systems.

distillation at 196–8°C.²⁶ Then, a molar ratio of 2 : 1 of benzoyl chloride (90 mL) to AAc (27 mL) was used to form **1**, which was purified from a reactive fractional distillation at 73–5°C.²⁷ To prevent the generation of radicals during the procedure, a low amount of hydroquinone (1 w/v %) was added to the distillation flask and to the final product. The molecular structure of the pure product **1** was corroborated by ¹H-NMR spectrometry with a 6 mg/mL solute solution.

¹H-NMR (CDCl₃, 400 MHz, δ , ppm): 6.65 (d, $J_{\text{trans}} = 16.81$ Hz, 1H, *H—CH=CH—), 6.36 (dd, 1H, —CH*=CH₂), 6.20 (d, $J_{\text{cis}} = 10.04$ Hz, 1H, *H—CH=CH—). NMR coupling constant (J) for trans (J_{trans}) or cis vicinal protons (J_{cis}) present in alkenes.

Synthesis of Vinyl Monomer 3

Monomer **3** was obtained with a friendly synthesis process optimized in our laboratory (Scheme 3). The reaction conditions, such as the concentration of sodium carbonate buffer (2.5, 5, 10, 15, and 20 w/v %), and the reaction time (4 or 24 h) were examined to establish the best reaction conditions. In all cases, a general procedure similar to that described as follows was used. In an Erlenmeyer flask, **2** (3.516 g, 0.02 mol) was dissolved in a buffer solution of sodium carbonate (40 mL) and placed in an ice bath, where the system underwent a temperature reaction close to 3°C. Afterward, **1** (2.00 mL, 0.024 mol) was slowly dropped from a drop funnel into the reaction mixture with high stirring, with the temperature maintained for 10 min. The reaction was then kept at room temperature in the absence of light for a further 4 or 24 h. Finally, the reaction mixture was placed in a beaker, where sodium carbonate was precipitated under stirring by the addition of acetone. The supernatant was then separated, and the pH was adjusted to 2 by the addition of a 3M hydrochloric acid aqueous solution. The precipitation of monomer **3** took place after a new addition of acetone. The solid monomer that we obtained was washed three times with acetone under stirring and dried until it reached a constant mass. The characterization of the pure monomer **3** was carried out at room temperature through UV-vis, FTIR, and ¹H- and ¹³C-NMR spectrometry.

FTIR spectroscopy (KBr pellet, cm⁻¹): 3473 (ν O—H, —SO₃H), 3294 (ν N—H, —HN—CO—), 3111 and 3048 (ν C—H, CH₂=CH— and —C₆H₄—), 1665 (ν C=O, —HN—CO—), 1209 (ν_{as} S=O, —SO₃H). ¹H-NMR (D₂O, 400 MHz, δ , ppm): 7.65 (d, $J = 8.81$ Hz, 2H, —H^aC₆H₃—), 7.50 (d, $J = 8.80$ Hz, 2H, —H^bC₆H₃—), 6.26 (dd, $J = 16.63$ Hz, 1H, —^cHC=CH₂), 6.20 (dd, $J = 9.78$ Hz, 1H, —HC=HC—H^d), 5.75 (dd, $J = 1.96$ Hz, 1H, —CH=HC—H^e). ¹³C-NMR (D₂O, 100 MHz, δ , ppm): 167 (—HN^aCO—), 139.9 (—HN—^bC), 138.7 (—O₃S—^cC), 130.3 (—HNCO—^dCH=CH₂), 129 (H₂^eC=CH—), 126.5 (—O₃S—C=^fH—), 121.3 (—HN—C=^gH—).

Formation of Linear Polymer 4

Vinyl monomer **3** was placed (3.00 g) in a beaker and solubilized in water (40 mL) under stirring at room temperature; we adjusted the solution at pH 8 with a 1M sodium hydroxide aqueous solution. Sodium persulfate (0.574 g) and sodium bisulfate (0.250 g) were poured into the reaction mixture with a molar ratio of 5 : 1 of monomer **3** to radical initiator under stirring for 1 h at 50°C (Scheme 3). A 3M chlorhydric acid aqueous solution (20 mL) was

added to the reaction mixture, and the polymer was then precipitated by acetone addition (80 mL) at room temperature, and the supernatant was eliminated. Polymer **4** was washed under stirring once more with an excess of acetone and dried until it reached a constant mass. The proton-ion content per gram of dry polymer was finally attained through an acid–base titration with phenolphthalein as an indicator.

FTIR spectroscopy (KBr pellet, cm⁻¹): 3451 (ν O—H, —SO₃H), 3312 (ν N—H, —CONH—), 2925 (ν C—H, —CH₂—CH—), 1920 (σ C—H, H—Ph), 1676 (ν C=O, —CONH—), 1209 (ν_{as} S=O, —SO₃H). ¹H RMN (D₂O, 400 MHz) δ (ppm): 9.78 (1H, —SO₃H^a), 7.38 (2H, H^b—Ph), 7.11 (2H, H^c—Ph), 2.23 (1H, —CH^d—CO—), 1.58 (2H, —CH₂^e—CH—).

Synthesis of Biodiesel from Acid Catalysis

The esterification reaction of oleic acid with short-chain aliphatic alcohols was investigated with the sulfonyl group present in the repetitive unit of polymer **4** as a solid acid catalyst. Several reaction conditions were analyzed; these conditions included the use of primary alcohols with different alkyl chains, catalyst content, temperature, and reusability testing. The biodiesel formation was verified from an acid–base titration of the remaining proton ions of the fatty acid in the reaction mixture as a function of time. When the esterification yield was near 100%, the polymer was recovered by filtration, and the alcohol excess in the liquid sample was evaporated. The biodiesel formed was then characterized by FTIR and ¹H-NMR spectrometry.

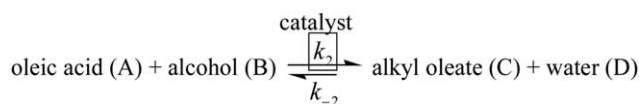
Effect of the Alcohol Molecular Structure on the Esterification Reaction. A mixture consisting of oleic acid (2.00 g), an alcohol such as methanol, ethanol, or 1-propanol and the polymer (0.1466 g) containing sulfonyl groups were incorporated into a reflux system with a molar ratio of 100 : 1 of alcohol to oleic acid. In all cases, a catalyst content of 5 mol % with regard to oleic acid was used. The formation of biodiesel took place at 5°C below the boiling point of the alcohol, and the esterification performance as a function of time was followed through acid–base titration until a constant value was reached.

Influence of the Catalyst Content and Temperature on Biodiesel Formation. With a procedure similar to the previously described one, the effect of the catalyst content (0, 5, 7.5, or 10 mol %) on the esterification yield was analyzed when a 100 : 1 molar ratio of methanol (28.60 mL) to oleic acid (2.00 g) was reacted at 60°C. The reaction evolution was followed by acid–base titration until the esterification reaction reached its plateau. Moreover, each reaction was assayed at least twice to obtain an average value, which was compared to those reference values achieved when 98 wt % sulfuric acid was used as the catalyst (10 mol %). The influence of the temperature (40, 42, 45, 50, 55, 57, and 60°C) on the performance of oleic acid esterification with methanol and 10 mol % catalyst was also examined.

On the other hand, the swelling degree of polymer **4** was determined when a dry sample (10 mol %) with a particle size range of 0.2–0.4 mm was left in contact with the reaction mixture in a graduated tube for 24 h at 25°C. The equilibrium volume swelling ratio was determined from the bulk volume of the sample in the swollen equilibrium state relative to that found in the

dry state.²⁸ After centrifugation of the heterogeneous mixture, the supernatant was eliminated, and the swollen polymer mass was recorded in a digital balance (Shimadzu LIBROR EB-3200D, Japan). In addition, the mass of liquid retained by the polymer could be also determined. These assays were carried out at least three times.

Analytical Procedure. The esterification reaction between oleic acid and the alcohol is represented as follows:



The conversion of oleic acid (χ ; %) was calculated according to eq. (1):

$$\chi = \left(1 - \frac{\alpha_t}{\alpha_0}\right) \times 100 \quad (1)$$

where the acidity value (α) of a sample of the reaction mixture is determined through acid–base titration at the beginning (α_0) and for a given reaction time (α_t). The former was expressed as moles of proton ions per gram of sample.

Reusability Testing. The performance of the catalyst after it was used several times was investigated to confirm its reusability for biodiesel formation. The esterification reaction between oleic acid and methanol catalyzed by sulfonyl groups took place at 60°C, where a 100 : 1 molar ratio of alcohol to fatty acid and a 10 mol % of catalyst were used. After the reaction was completed, the solid catalyst was recovered from the reaction mixture by centrifugation. As a side reaction, the halide ions present as an impurity in the reaction were converted into hydracids because of the fact that the sulfonic acid exhibited a higher acidity. Generally, these hydracids are gases solubilized into the reaction mixture that escape from the reactor; this inactivates the catalyst through the formation of sulfonate groups onto polymer chain. Therefore, the latter are reconstituted to the acid form by mixing with 3M hydrochloric acid in methanol, where a 40 : 1 mass ratio from acid solution to solid was used under stirring at 25°C for 1 h. The mixture was centrifuged again, and the catalyst was reused to esterify fresh oleic acid for biodiesel production. A known quantity of fresh methanol was also added to the reaction mixture to compensate for the methanol consumed in the reactor. In each reuse cycle, the oleic acid conversion in the reaction mixture was determined by colorimetric titration.

Characterization of the Biodiesel Molecules

The reagent oleic acid and the synthesized alkyl esters were characterized by FTIR and ¹H-NMR spectroscopy. For biodiesel, at the end of the reaction, a sample of the product was taken, and the excess alcohol and water generated were evaporated until a constant mass was reached. The liquid sample was supported on a silver bromide pellet, and the FTIR spectrum was obtained. The spectrum of oleic acid showed the following characteristic bands: 3430–2520 cm⁻¹ (ν O–H broad band, –CO₂H) and 1710 cm⁻¹ (ν C=O, –CO₂H). The alkyl esters displayed the vinyl group band at 3010 cm⁻¹ (ν C–H,

–CH₂=CH–), signals at 2925 and 2854 cm⁻¹ (ν C–H, hydrocarbon backbone), and a signal close to 1740 cm⁻¹ (ν C=O, ester group). The ¹H-NMR spectra of the biodiesel and oleic acid were recorded at room temperature at a concentration near 6 mg/mL.

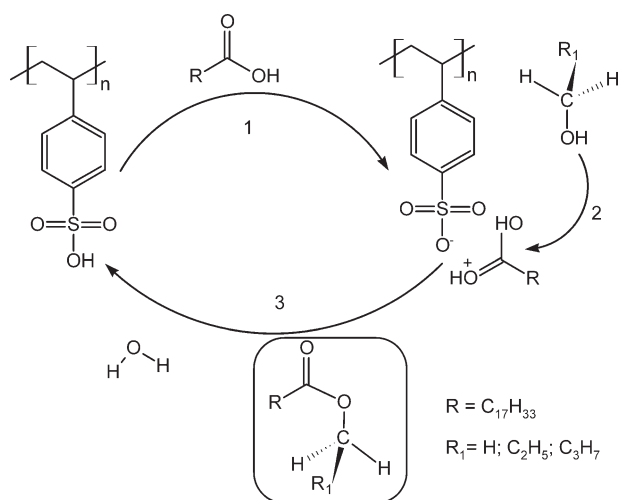
¹H-NMR (CDCl₃, 400 MHz, δ , ppm): Oleic acid: 5.37 (m, 2H, –CH=CH–), 2.39 (t, 2H, –CH₂–CO–), 2.04 (m, 4H, –CH₂*–CH=), 1.67 (m, 2H, –CH₂*–CH₂–CO–), 1.32 (m, 20H, –CH₂–CH₂–), 0.90 (t, 3H, –CH₂–CH₃*). Methyl oleate: 5.31 (m, 2H, –CH=CH–), 3.63 (s, 3H, –OCH₃), 2.27 (t, 2H, –CH₂–CO–), 1.99 (m, 4H, –CH₂*–CH=), 1.60 (m, 2H, –CH₂*–CH₂–CO–), 1.26 (m, 20H, –CH₂–CH₂–), 0.86 (t, 3H, –CH₂–CH₃*). Ethyl oleate: 5.36 (m, 2H, –CH=CH–), 4.14 (q, 2H, –O–CH₂*–CH₃), 2.30 (t, 2H, –CH₂–CO–), 2.02 (m, 4H, –CH₂*–CH=), 1.63 (m, 2H, –CH₂*–CH₂–CO–), 1.28 (m, 23H, –CH₂–CH₂– and –O–CH₂–CH₃*), 0.90 (t, 3H, –CH₂–CH₃*). Propyl oleate: 5.33 (m, 2H, –CH=CH–), 4.02 (t, 2H, –O–CH₂*–CH₂–CH₃), 2.28 (t, 2H, –CH₂–CO–), 2.02 (m, 4H, –CH₂*–CH=), 1.63 (m, 4H, –CH₂*–CH₂–CO– and –O–CH₂–CH₂*–CH₃), 1.28 (m, 20H, –CH₂–CH₂–), 0.93 (t, 3H, –O–CH₂–CH₂–CH₃*), 0.87 (t, 3H, –CH₂–CH₃*).

RESULTS AND DISCUSSION

One of the greatest challenges of polymer science today concerns the ability to understand the structure–property relationship of a particular polymer system for adequately predicting its use in a technological application. In addition, the physicochemical properties of a given polymer depend mainly on its molecular structure and the spatial arrangement of its chains.^{29–33} The polymer chain length and functional groups of its repeating unit are factors that have a relevant impact on its properties and potential applications. Although it is known that Bronsted and Lewis acids have catalytic activity during esterification and transesterification reactions, the selection and building of a successful catalyst for a reaction in a heterogeneous system still need to be researched. In this study, we proposed the synthesis of polymer **4** from a radical polymerization of monomer **3**, whose molecular structure contained a sulfonyl group. This strong acid was able to provide a proton ion to the reaction center, catalyzing the esterification of oleic acid (Scheme 4). Therefore, this insoluble polymer was used as a heterogeneous catalyst in the study of the formation of biodiesel from the esterification reaction of oleic acid and primary alcohols.

Synthesis of the Vinyl Monomer and Its Polymer

The synthesis of monomer **3** was carried out from the reaction of **1** and **2** in a basic aqueous solution under stirring at room temperature (Scheme 3), where the effect of the buffer concentration and the reaction time were studied. The evolution of the reaction yield (Y_{ester}) was followed by ¹H-NMR spectroscopy with an internal standard in the sample. The integral value corresponding to the characteristic sign of product **3** (6.26 ppm, 2H) and byproduct acrylate (5.65 ppm, 1H) was referenced to the aromatic protons of benzoic acid, which appeared at 7.83 ppm (2H). Figure 1 shows the influence of the buffer concentration on the formation of product **3** for 4 h of reaction. We



Scheme 4. Proposed mechanism for the catalyzed oleic acid esterification: activation of the electrophile by complex formation (1), nucleophilic attack of alcohol to the activated carbonyl group (2), and formation of the products and regeneration of the catalyst (3).

found that using a 1.2 : 1 molar ratio from **1** to **2**, monomer **3** yielded its maximum value (87 mol %) when a 10 w/v % carbonate solution was used. This behavior indicated the existence of an optimum buffer concentration, where a pH value near 8.5 determined a higher content of the free amine **2** and, thus, its exclusivity as a strong nucleophile in the reaction (Scheme S1, Supporting Information). In addition, when the buffer concentration was lower than 10 w/v % (Figure 1), the capacity buffer was not able to retain a high enough free amine content. Therefore, the water molecule prevailed as the most abundant nucleophile in the reaction (Scheme S1, Supporting Information). However, a buffer concentration higher than 10 w/v % resulted in an increase in the hydroxyl group content, a strong nucleophile that contributed to the hydrolysis reaction of reagent **1**. The reaction performance yielded 98 mol % of product **3** when a 1.2 : 1 molar ratio and a 10 w/v % buffer concentration were used under stirring for 24 h. This behavior arose from the fact

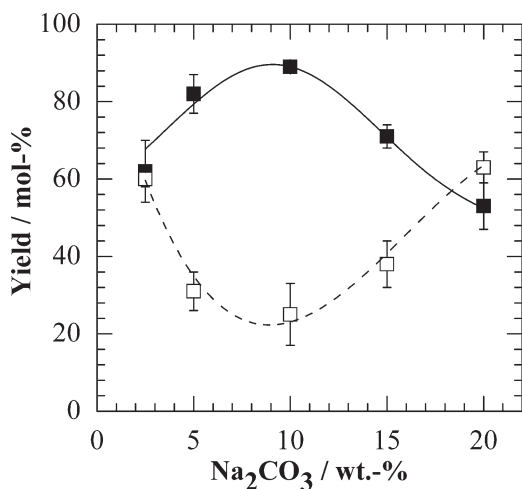


Figure 1. Influence of the sodium carbonate concentration on the formation of (■) vinyl monomer **3** and (□) sodium acrylate as the byproduct after 4 h of reaction.

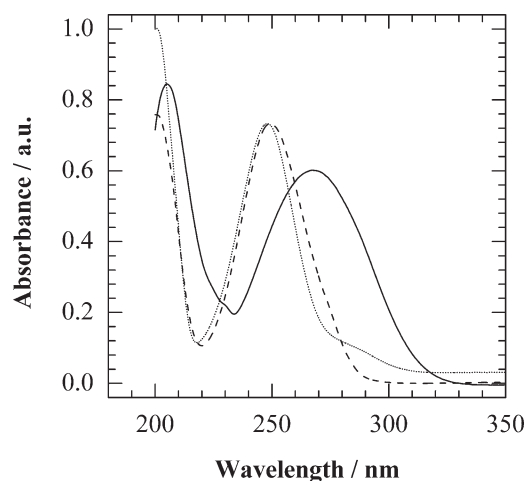


Figure 2. UV-visible spectrophotometry. Spectral curves of a (.....) **2** aqueous solution, (—) monomer **3**, and (- - -) polymer **4**.

that a longer time allowed the system to reach its equilibrium state, where a total conversion of reagent **2** and less sodium acrylate were obtained. Subsequently, the double bond of this molecule was polymerized in aqueous solution at pH 8, where the reactive mixture of sodium persulfate and sodium bisulfate generated radicals through an oxide-reduction reaction. The polymer generated at 50°C after 1 h of reaction was purified by precipitation with acetone. The polymerization yield was about 95 mol %. Monomer **3** and its polymer were characterized by UV-vis spectrophotometry and FTIR and ¹H-NMR spectrometry. The UV-vis spectrum of monomer **3** was recorded in an aqueous solution, where it was possible to observe (Figure 2) a maximum absorption band at 271 nm attributed to the $\pi \rightarrow \pi^*$ transition of the conjugated electron system. Product **3** showed a bathochromic shift of the maximum absorbance with regard to the initial reagent **2** ($\lambda_{\text{max}} = 250 \text{ nm}$); this demonstrated the formation of a product with a conjugated π -electron system longer than that of **2** (Scheme 3 and Figure 2).

Moreover, the reaction of the double bond of monomer **3** yields product **4**, whose maximum absorbance occurs at 249 nm. The latter showed a spectral curve similar to that of reagent **2** because both compounds had the same chromophore. The formation of polymer **4** was corroborated by FTIR spectroscopy from the disappearance of the double-bond band at 1633 cm^{-1} of monomer **3** (Figure S1, Supporting Information) and the shift of the carbonyl signal toward a higher wave number (from 1661 to 1680 cm^{-1}). In addition, the molecular structure of monomer **3** was confirmed from ¹H-NMR spectrometry by the correlation between the integrals and shifts assigned to each type of proton (Figure S2, Supporting Information). The signals corresponding to the aromatic protons appeared at 7.65 and 7.50 ppm, whereas the system of vinyl protons was found between 6.32 and 5.74 ppm. Additionally, the ¹H-NMR spectrum of polymer **4** showed broad signals assigned to the sulfonyl group at 9.79 ppm and the aromatic protons between 7.40 and 7.00 ppm and the appearance of aliphatic protons at 2.22 and 1.58 ppm (Figure S3, Supporting Information). The amount of sulfonyl groups was determined from acid-base titration, attaining a content of proton ions near 2.6 mmol/g of

dry polymer **4**. In addition, $^1\text{H-NMR}$ spectrometry was used as a tool of quantification, where the polymer showed a protonation percentage of repetitive units close to 85 mol %. This value was achieved from the integration of the sulfonyl group signal at 9.79 ppm in relation to its four aromatic protons at 7.39 and 7.09 ppm (Figure S3, Supporting Information). The full report for each technique is provided in the Experimental section.

Study of the Biodiesel Formation with an Acid Catalyst

The accessibility of acid sites and acid strength are important properties that are usually investigated for catalysts. It is known that the insertion of a phenyl group within the organosulfonic acid leads to an increase in the acidity of the sulfonyl group.²⁴ In addition, the incorporation of hydrophobic organic groups into the organosulfonic acid functionalized support selectively created an unsuitable environment for water, and this led to its exclusion from the active site. When the esterification reaction took place in the reaction mixture, the reactants were catalyzed by the organosulfonic acids, and those produced water molecules were excluded from the catalytic site by the hydrophobic aromatic ring. These factors are considered in the design of a catalyst whose structure–activity relation allows it to reach the highest esterification performance. In addition, the electron-withdrawing amide group stabilized the sulfonate group negatively charged by an inductive effect, and this contributed to the acidity of the sulfonyl group in polymer **4**. Therefore, this catalyst was synthesized and examined in the esterification of oleic acid, where a 100 : 1 molar ratio of alcohol to oleic acid was used to secure first-order reaction kinetics. Here, the influence of the catalyst content, temperature, and molecular size of alcohol on the performance of esterification reaction was analyzed.

Kinetic Model. For the esterification of oleic acid [eq. (1)], the apparent reaction rate can be described as follows:

$$-\frac{dc_A}{dt} = k_2 c_A^a c_B^b - k_{-2} c_C^c c_D^d \quad (2)$$

reaction components such as “A”, “B”, “C” and “D” are defined above in *analytical procedure*, where a , b , c , and d refer to their reaction orders and k_2 and k_{-2} are the kinetic constants for the forward and reverse reactions, respectively.³⁴ Because a large excess of methanol (100 times greater than that of oleic acid) in the reaction mixture was used, nonreversible pseudo-first-order reaction kinetics were expected. Therefore, the value of k_2 had to be much greater than that of k_{-2} ; this was in agreement with Le Chatelier’s principle. Also, because of the fact that the methanol content does not vary significantly with the reaction evolution ($k_2 c_B^b = k_1$, where k_1 is the rate constant), the previous equation can be simplified as follows:

$$-\frac{dc_A}{dt} = k_1 c_A^a \quad (3)$$

When $a = 1$, eq. (3) can be integrated into the following expression:

$$c_A = c_A^0 \exp(-k_1 t) \quad (4)$$

Where the superscript 0 highlights the initial concentration of oleic acid. Because reaction yield (Y_{ester}) is directly related to χ ($Y_{\text{ester}} = \chi$), the decrease in the concentration of proton ions (α) in the system followed by acid–basic titration can be used to

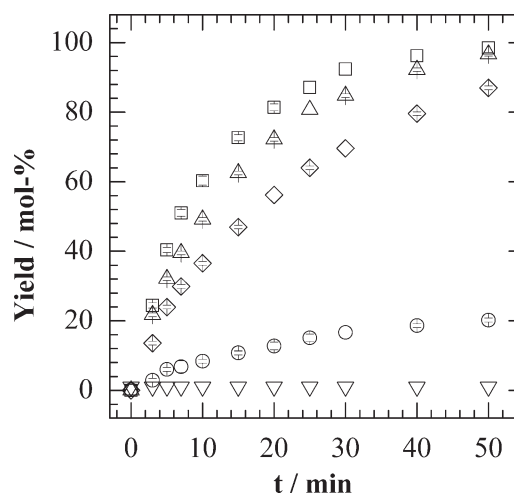


Figure 3. Influence of the catalyst content on the oleic acid esterification with methanol against a time (t) function. Percentages of (∇) 0, (\diamond) 5, (Δ) 7.5, and (\square) 10 mol % pendant sulfonic acid onto polymer **4** were used in the reaction mixture. In addition, the (\circ) commercial resin Permutit Q with a 10 mol-% of catalyst was researched.

measure the reaction kinetics. The replacement of eq. (4) in eq. (1) leads to eq. (5), and this allows the determination of the value of the experimental rate constant:

$$Y_{\text{ester}} = 1 - \exp(-k_1 t) \quad (5)$$

Effect of the Catalyst Content on the Performance of Oleic Acid Esterification. The catalyst-support system containing 0, 5, 7.5, or 10 mol % sulfonyl groups, together with a 100 : 1 molar ratio of methanol to oleic acid, was used to generate methyl oleate at 60°C. The FTIR spectra corresponding to oleic acid and methyl oleate attained at the end of the esterification reaction showed that the carbonyl band in the acid (1707 cm^{-1}) shifted toward a higher wave number; this supported the formation of ester groups (Figure S4, Supporting Information). Biodiesel formation was also followed by $^1\text{H-NMR}$ spectrometry from the integral value of the O -methyl signal (3.63 ppm, 3 H) with regard to the two α protons of the carbonyl group at 2.27 ppm (Figure S5, Supporting Information). In this study, we found that during oleic acid esterification, a higher catalyst content led to a faster reaction rate (Figure 3). For 10 mol % catalyst, the reaction reached its maximum yield (close to 98%) at 20 min, whereas with 7.5 mol % catalyst, the plateau was observed at 50 min. Esterification reactions with 5 mol % sulfonyl groups achieve their maximum conversion after 50 min of reaction. No reaction occurred without the presence of the catalyst in the reaction mixture; this supported the fact that autocatalysis was not significant at those conditions. When the proton ion attached to the oxygen atom of the carbonyl group, the carbon atom of the carbonyl group showed improved ability as an electrophile (Scheme 4). Therefore, a higher catalyst concentration in the reaction mixture led to an increase in the content of activated carbonyl groups; this resulted in much faster reaction kinetics. In reference to the kinetic model, a pseudo-homogeneous pseudo-first-order behavior was assumed for the fitting of the reaction kinetics (Figure S6, Supporting Information). This has already been applied successfully by other

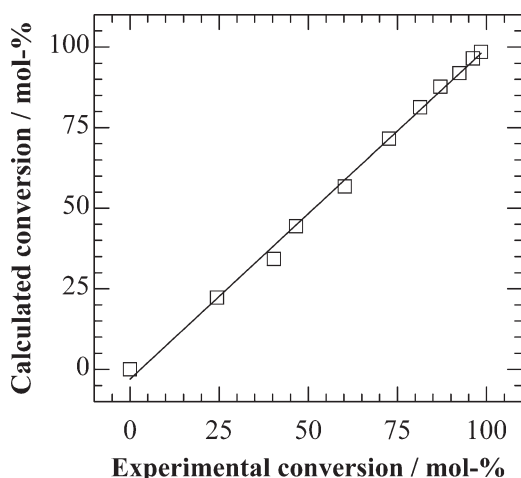


Figure 4. Correlation curve found between the data of the experimental conversion and those calculated for the esterification reaction with methanol at 60°C when a pseudo-first-order reaction was considered ($R^2 = 0.997$).

authors to the pre-esterification kinetics of free fatty acids in vegetable oil with the aid of acid-ion-exchange resins.³⁵ Figure 4 shows a good correlation ($R^2 > 0.99$) between the experimental and calculated values of oleic acid conversion when a 10 mol-% of catalyst was used. This behavior supported the hypothesis that a kinetic model described by a pseudo-homogeneous non-reversible pseudo-first-order reaction is a suitable and reliable way to calculate the rate constants. Moreover, the turnover frequency (TOF; s^{-1}) based on the constant k_1 could be obtained from eq. (6), where $\eta_{0,FFA}$ is the initial molar content of oleic acid and η_{H^+} is the exchange capacity of the catalyst:³⁵

$$TOF = k_1 \frac{\eta_{0,FFA}}{\eta_{H^+}} \quad (6)$$

Table I reveals that an average value of TOF near $1.40 \times 10^{-2} s^{-1}$ was attained for methyl oleate when the catalyst content of polymer **4** varied from 5 to 10 mol %. This behavior supported the assumed hypothesis stated previously that the heterogeneous

Table I. Formation Rates of Biodiesel with Different Reaction Conditions

Catalyst (mol %) ^a	TOF (s^{-1}) ^b		
	Ethanol	Methanol	1-Propanol
5 ^c	3.70×10^{-3}	1.37×10^{-2}	1.12×10^{-3}
7.5 ^c	—	1.43×10^{-2}	—
10 ^c	—	1.40×10^{-2}	—
10 ^d	—	9.40×10^{-4}	—
10 ^e	—	2.00×10^{-2}	—

^a Content of sulfonic acid relative to the carboxyl groups of the oleic acid.

^b Average value of the TOF obtained from eq. (6).

^c Sulfonyle groups present in polymer **4** ($\eta_{H^+} = 2.6 \times 10^{-3}$ mol/g).

^d Permutit Q, a cation-exchange resin with a proton-ion capacity of 4.2×10^{-3} mol/g.

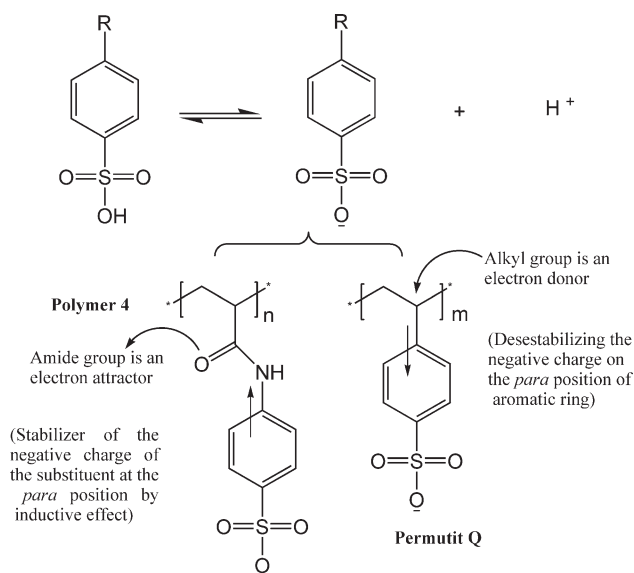
^e Esterification reaction catalyzed by sulfuric acid (98 wt %, homogeneous system).

catalyst did not exhibit mass restriction and adsorption/desorption effects during the reaction. This phenomenon agreed with the fact that this catalyst, an insoluble linear polymer with a small particle size (20–40 mesh), led to esterification kinetics that were similar to those found in a homogeneous system. Several factors govern the catalyst performance; these included poor adsorption of the reagents onto the aromatic ring in the repetitive unit and also the fact that a smaller particle size led to a higher catalyst surface and favored the interaction reagent–reaction center. Moreover, one should not dismiss the fact that the volume of the catalyst particle expanded about 30 ± 2 vol % by swelling in the reaction mixture, where some polymer chains were mainly solvated by alcohol molecules. Hydrogen bonding between amide groups of the chains generated no covalent crosslinking point, and this led to gel formation in the swollen state. Thus, large spaces were generated into the gel skeleton, and this contributed to the diffusion of reagents to the sulfonyl group. On the other hand, when the catalytic activity of polymer **4** was compared with that shown by Permutit Q, the former exhibited a TOF value that was 15 times higher than that obtained with the sulfonyl-group-functionalized commercial resin (Table I). Although in both cases esterification took place in a heterogeneous system, Permutit Q seemed to exhibit a limited phenomenon of mass transfer. Furthermore, we could not disregard the fact that the repetitive unit of every polymer presented different molecular structures. The amide group in polymer **4** (Scheme 5) was an electron-withdrawing group that increased the acidity of phenyl sulfonic acid because, during its dissociation, the former better stabilized the negative charge of the sulfonate group as compared to that of Permutit Q. Thereby, polymer **4** clearly showed very good performance as a catalyst, where its TOF value for methanol was 0.7 times that found for sulfuric acid (Table I). This was a high esterification rate when we took into account the fact that sulfuric acid worked in a homogeneous system.^{36,37}

Variation of the Reaction Temperature: Determination of the Kinetic Parameters. Figure 5 shows the results achieved from esterification reactions carried out with 10 mol % sulfonyl group at different temperatures and an initial molar ratio of 100 : 1 of methanol to oleic acid. It was clear that the reaction rate increased significantly with temperature because the molecules in the reaction mixture had a higher kinetic energy, which favored the access of reagents to the reaction center. In addition, Table II shows several rate constants determined at different temperatures with nonlinear least-squares minimization, where a pseudo-homogeneous pseudo-first-order behavior was assumed for the fitting of the data. In all cases, the value found for R^2 was higher than 0.985; this indicated that eq. (5) fit the experimental data well. These values were then used to calculate the pre-exponential factor (A) and the activation energy (E_a) through the Arrhenius equation [eq. (7)]:

$$\ln k_2 = -\frac{E_a}{RT} + \ln A \quad (7)$$

Figure 6 displays the Arrhenius plot of the second-order forward rate constants recorded at seven temperatures (T) in the range 40–60°C. The value of E_a estimated from the slope of the Arrhenius plot was $(40 \pm 1) \text{ kJ} \cdot \text{mol}^{-1}$ when a value of



Scheme 5. Influence of the substituent attached to the aromatic ring on the acidity of sulfonic acid. The electron-attractor substituent stabilized the conjugated base and thus increased the acidity of its conjugated acid.

$8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for gas constant (R) was used, and a value of $(101 \pm 1) \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$ was obtained for A .

This value of the apparent E_a agreed with that obtained by Bhatia *et al.*³⁸ (40.77 kJ/mol) for the esterification of palmitic acid with isopropanol over a *p*-toluene sulfonic acid catalyst. However, the E_a reported by Tesser *et al.*³⁹ for the esterification of olein (fatty acids) with methanol over Relite CFS (a commercial acid-exchange resin) was 53 kJ/mol . The disparity found between those authors may have been due to difference in the reaction systems and the catalyst used in this study.

Esterification Performance Against the Molecular Structure of the Alcohol. The influence of the alkyl chain of primary alcohols, such as methanol, ethanol, and 1-propanol, was analyzed on esterification rates. Because the formation of bubbles during

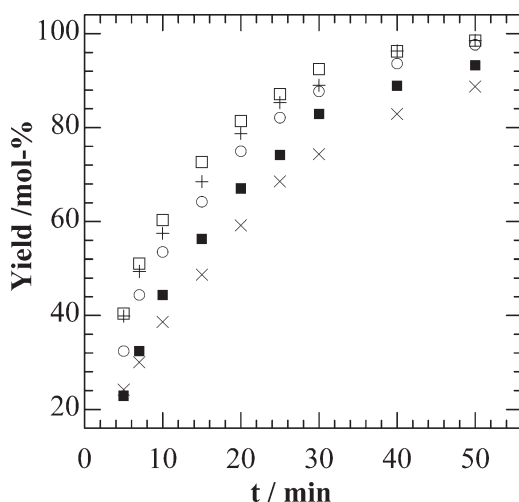


Figure 5. Esterification performance for a 10 mol-% of catalyst against time (t) when a 100 : 1 molar ratio from methanol to oleic acid was used at (x) 45, (■) 50, (○) 55, (+) 57, or (□) 60°C (white square).

Table II. Esterification Rates of the Oleic Acid Determinants at Different Temperatures

T ($^{\circ}\text{C}$)	k_1 (s^{-1})	R^2
40 ± 1	$(5.70 \pm 0.02) \times 10^{-4}$	0.987
42 ± 1	$(6.30 \pm 0.02) \times 10^{-4}$	0.992
45 ± 1	$(7.20 \pm 0.01) \times 10^{-4}$	0.995
50 ± 1	$(9.20 \pm 0.02) \times 10^{-4}$	0.985
55 ± 1	$(1.14 \pm 0.02) \times 10^{-3}$	0.991
57 ± 1	$(1.28 \pm 0.04) \times 10^{-3}$	0.997
60 ± 1	$(1.40 \pm 0.02) \times 10^{-3}$	0.993

The observed k_1 was obtained from a nonlinear least-square minimization.

reflow caused a variation in the reagent concentration and this led to errors in the measurement of the reaction kinetics, boiling in the system needed to be avoided. Therefore, a 100 : 1 molar ratio of the alcohol to oleic acid was used under stirring with 5 mol % catalyst at 5°C below the alcohol boiling point. Although the boiling point of methanol was lower than that found in other alcohols, the former achieved its maximum yield close to 98 mol % at a time shorter than 80 min (Figure S7, Supporting Information). This behavior showed a prevalence for steric impediment over the thermal effect of the system, where a smaller alkyl chain in the molecular structure of the alcohol resulted in a faster esterification kinetics. Table I also illustrates the TOF value for biodiesels obtained from different alcohols, which decreased as follows: Methanol > Ethanol > Propanol. Clearly, the nucleophilic power of the alcohol was controlled by the size of its alkyl chain, which governed the alcohol's ability as a nucleophile. The phenyl sulfonic acid, a Bronsted–Lowry acid as strong as sulfuric acid, has been widely demonstrated to be able to promote a significant esterification rate with promising results.

Reusability of the Catalyst. This study was developed to determine the performance of the catalyst after it was used in several esterification cycles. Figure 7 shows that the yield of biodiesel after the third cycle is lower than that found for the fresh

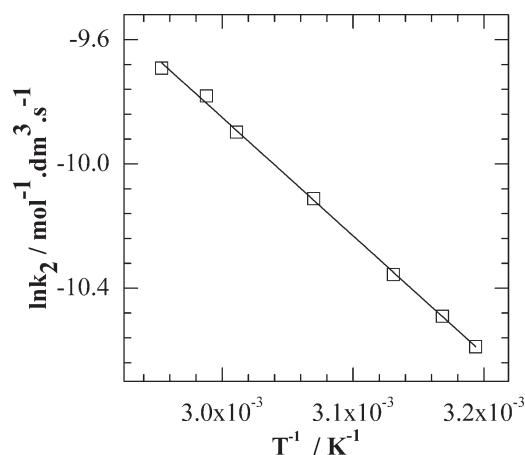


Figure 6. Arrhenius plot of the second-order forward rate constants vs. reciprocal temperature (T^{-1}), attained for methyl oleate formation over polymer 4 with a 10 mol-% of catalyst.

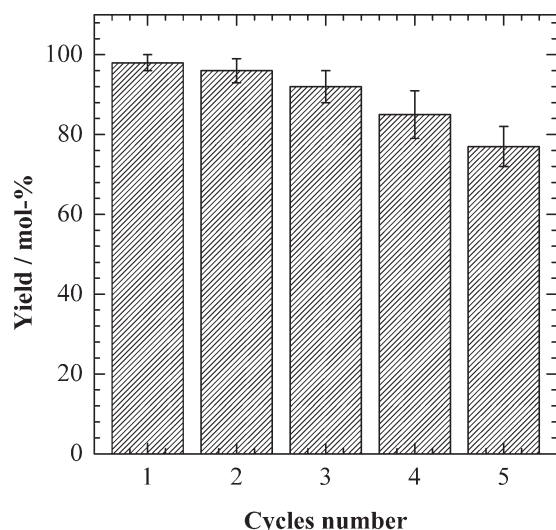


Figure 7. Number of cycles where 10 mol % catalyst was successful in catalyzing biodiesel formation at 60°C.

catalyst. The biodiesel yield remained at 85 mol % when the catalyst was used for the fourth time, whereas the former decreased to a 77 mol % after five successive uses. Therefore, this catalyst exhibited a successful performance for esterification reactions at least to a fifth time of successive use, and this makes to the catalyst promising on an industrial scale.

CONCLUSIONS

A solid acid catalyst was prepared in excellent yield from the synthesis of a sulfonyl-group-functionalized vinyl monomer and its polymerization in aqueous solution. The catalytic activity of the pendant sulfonyl group to polymer backbone was then verified in a heterogeneous system for oleic acid esterification against a primary alcohol. Here, methanol exhibited the highest yield for relatively short reaction times. The increase in the sulfonyl group content led to faster esterification kinetics. Moreover, the highest yield of methyl oleate (98 mol %) was reached after 20 min of reaction when 10 mol % catalyst was used. In addition, a regular value of TOF near $1.4 \times 10^{-2} \text{ s}^{-1}$ was achieved for methanol when the catalyst content was varied from 5 to 10 mol %. This phenomenon supported the fact that the catalyst did not show mass restriction and adsorption/desorption effects and also showed a performance similar to that found for a homogeneous system. This result may have been due to a higher specific surface area given by a smaller catalyst particle size; this favored the interaction reagent–reaction center. Moreover, the adsorption of reagents onto the aromatic ring of the polymer repetitive unit was apparently poor. However, the diffusion of reagents to the sulfonyl group may have been facilitated by the swelling of catalyst particles where some polymer chains were mainly solvated by alcohol molecules. Therefore, a pseudo-homogeneous nonreversible pseudo-first-order kinetics proved to be a suitable model for the description of the reaction rates observed. When different primary alcohols were compared, a larger chain length led to slower reaction kinetics. The alcohol performance as a nucleophile increased with the decrease in the steric hindrance. The pendant aryl sul-

fonic acid on the polymer backbone demonstrated the ability to promote a high reaction performance of oleic acid esterification in a heterogeneous system. This behavior confirmed the fact that the sulfonyl group was a Bronsted–Lowry acid as strong as sulfuric acid, where the amide group enhanced the acidity of the sulfonyl group. All these results demonstrate that polymer **4** exhibited a significant esterification rate at least to a fifth successive use in addition to a promising performance as a catalyst for heterogeneous reactions.

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