



Research Article

A Novel Green Synthesis Method of Poly (3-Glycidoxypropyltrimethoxysilane) Catalyzed by Treated Bentonite

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Abstract

The present work focuses on the preparation and characterization of poly(3-Glycidoxypropyltrimethoxysilane) (PGPTMS) under mild conditions. Ring-opening polymerization of the 3-Glycidoxypropyltrimethoxysilane (GPTMS) is initiated with the bentonite of Maghnite-H⁺ (Mag-H⁺), an ecologic and low-cost catalyst. The evolution of epoxy ring-opening was studied in bulk and in solution using CH₂Cl₂ as solvent, as well as the influences of several factors, such as the amount of Mag-H⁺, polymerization time and temperature on the yield of polymer were investigated. The best polymer yield (30 %) was obtained in bulk polymerization at room temperature (20 °C) for a reaction time 8 h, and it's increases with time and reaches 68 % for 7 days. The structures of the obtained polymers (PGPTMS) were confirmed respectively by Fourier transform infrared spectroscopy (FT-IR) and nuclear magnetic resonance (NMR). The thermal properties of the prepared polymers were given by Differential Scanning Calorimetry (DSC) and thermogravimetric analysis (TGA), the *T_g* of PGPTMS is recorded at -31.27 °C, and it is thermally stable with a degradation start temperature greater than 300 °C, all decomposition stopped at 600 °C. Copyright © 2020 BCREC Group. All rights reserved

Keywords: Cationic Ring-opening Polymerization; 3-Glycidoxypropyltrimethoxysilane; Montmorillonite; Mag-H⁺; Eco-catalyst

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1. Introduction

As is known, the 3-Glycidoxypropyltrimethoxysilane (GPTMS) is one of the most used coupling agents in the field of surface conversion treatment, while respecting the environment [1-3]. Hybrid organic-inorganic compounds prepared by the opening of epoxy ring of GPTMS [4-8] are known for their improved mechanical strength and thermal stability [9].

These hybrid inorganic-organic materials have important applications in many different areas, such as: protective membranes for organic polymers [10], anticorrosion coatings, chemical and plastics filters for space applications, optical waveguides [11,12] and limiting [13-16], optical amplification [17]. New types of contact lens [18] are prepared with these materials. Several synthesis of these organosilanes, via sol-gel method, using an acid [19,20] or a basic [21,22] as a catalyst were realized. Hydrolysis and silanol groups are formed with acid catalyst while hydrolysis proceeds take place simultane-

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ously with condensation with basic catalyst [23]. GPTMS derived hybrid materials were synthesized by TiCl_4 , in nonhydrolytic conditions, to achieve epoxy ring opening polymerization by a multistep reaction, linear compounds of different lengths and an inorganic network were formed by hydrolysis [24] and condensation reactions. Different amounts of BF_3OEt_2 , used to catalyze the organic polymerization of GPTMS affect the degree of inorganic cross-linking and the length of the ethylene oxide chains [25,26]. Other catalysts were used by other reviews as triethylamine [27] to produce a three-dimensional cross-linked elastomer. In previous work [28], a linear polyGPTMS and transparent polymer with great thermal resistance has been obtained with the Multi-metal cyanide (MMC) as a catalyst, under heating ($130\text{ }^\circ\text{C}$).

On the other hand, the influence of temperature on the hydrolysis of GPTMS has been studied by several authors [29]. Hydrolysis and condensation reactions accompanied with the opening of epoxy ring are favored with increase in temperature. As mentioned in the literature, the cationic polymerization of GPTMS cannot start without heating [4-8,28] such as the radical polymerization, the main purpose of this work is to use a simple and safe processing method without using high temperature to prepare a linear polyGPTMS with unhydrolysis alkoxy group. The polymerization reaction is realized under mild conditions, using a cationic catalyst, Mag-H^+ , an Algerian proton exchanged montmorillonite clay, in way to be in the context of green chemistry.

In a previous work [30], it has been shown that there is a correlation between acid activation of maghnite with different concentrations of H_2SO_4 and its catalytic activity. It has been found that the best results are obtained by acid activation with H_2SO_4 (0.25M) solution because the cationic exchange of maghnite by protons (Mag-H^+) is complete without destroying its structure. This solid catalyst is widely used in the ring-opening polymerizations as an effected catalyst with demonstrated results published in many international reviews [31-37], and has many advantages such as very low cost, the easy removal of the reaction mixture, regenerated by heating to a temperature above $100\text{ }^\circ\text{C}$ [31,32] compared to other catalysts.

In our work, we have explored a new method for a green synthesis of PGPTMS, by ring opening polymerization of GPTMS under mild conditions with the aim to respect the principles of green chemistry, without spend any energies. The polymerization reaction of GPTMS

is initiated with a green catalyst to replace electrophilic catalysts, such as: Brønsted and Lewis acids, which are very noxious and corrosive. The best results in term of transparency and yield of the product are obtained by the synthesis method in bulk. The structure of the obtained polymer (PGPTMS) was confirmed respectively by FTIR, $^1\text{H-NMR}$, and $^{29}\text{Si-NMR}$. The thermal properties of the prepared polymers were given by TGA analysis. The effects of different synthesis parameters, such as: the amount of Mag-H^+ , temperature and polymerization time, were discussed.

2. Materials and Methods

2.1 Materials

Raw-Maghnite (Algerian, natural montmorillonite clay), was procured from BENTAL (Algerian Society of Bentonites) and used as catalyst. The 3-glycidyloxypropyltrimethoxysilane (GPTMS) 98% used as monomer for synthesis PolyGPTMS, Dichlorométhane (CH_2Cl_2) 99.9 % used for the polymerization reaction and methanol 99 % analytical grad, used for precipitation. All these materials were used as received from SIGMA-Aldrich, without further purifications.

2.2 Structural Analysis

The chemical structure of the products was determined by Fourier transform infrared spectroscopy analysis (FTIR), converted from Perkin Elmer Two FT-IR with UATR sampling accessory. X-ray diffraction (XRD), conducted at room temperature by Bruker AXS D8 advanced X-ray diffractometer (40 kV, 30 mA) using $\text{Cu-K}\alpha$ radiation ($\lambda = 0.154\text{ nm}$) at the rate of 2° min^{-1} in the 2θ range of $2.0 - 80^\circ$. The $^1\text{H-NMR}$ and $^{29}\text{Si-MAS/NMR}$ (^{29}Si -Magic angle spinning/nuclear magnetic resonance) measurements were carried, using on an Avance Bruker NMR Spectrometer at 300 and 99.35 MHz, respectively. The spinning speed for cross-polarization magic angle spinning (CPMAS) was 4 MHz for ^{29}Si MAS NMR at room temperature. Chemical shift references are tetramethylsilane (TMS) and 4 mm zirconia rotor was used. Thermogravimetry (TGA) analysis, performed by PerkinElmer STA 6000 under air and nitrogen in the temperature range $20-800\text{ }^\circ\text{C}$ with a heating rate of $10\text{ }^\circ\text{C/min}$, the mass of the sample to be analyzed is 5–7 mg. Differential Scanning Calorimetry (DSC) analysis performed by universal VA.5A TA instrument, site average scan between $-100\text{ }^\circ\text{C}$ and $100\text{ }^\circ\text{C}$ with heating rate of $10\text{ }^\circ\text{C/min}$, using 6 mg of PGPTMS.

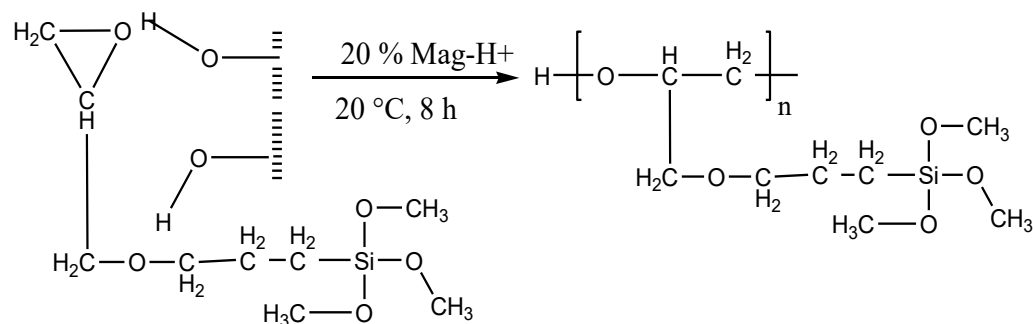
2.3 Preparation of the Mag-H⁺ Catalyst

Mag-H⁺ was prepared by a method similar to that described in our previous study [31,32]. The raw Maghnite was activated with a sulfuric acid solution (0.25 M) to give a Maghnite exchanged with protons, called Mag-H⁺. In an Erlenmeyer flask, 30 g of crushed raw Maghnite was dispersed in 1 L of distilled water. The mixture was stirred well during 2 h at room temperature, then left to settle for about 8 hours in a volumetric test tube until the appearance of Montmorillonite supernatant. After that about 100 mL of supernatant is taken and replaced by 100 mL of distilled water, the mixture is stirred again and left to settle for a second 8 hours. This operation is repeated until we recover the maximum of montmorillonite. To exchange the cation ions present in the clay by H⁺ ions, a solution of sulfuric acid H₂SO₄ (0.25 M) is added to the dried montmorillonite recovered. The mixture is maintained stirring for 48 hours, Then the catalyst (Mag-H⁺) formed, is filtered after being washed several times with distilled water up to pH 7. The Mag-H⁺ was dried in an oven for 24 h at 105 °C and then crushed. The catalyst structure is characterized by FTIR and XRD.

2.4 Procedures of Catalyst Synthesis

2.4.1 Ring-opening Polymerization of GPTMS

The ring-opening polymerization of 3-Glycidoxypropyltrimethoxysilane (GPTMS) was carried out in bulk and in solution using CH₂Cl₂ as solvent at various temperature and polymerization time, using various amounts of Mag-H⁺. The procedure was identical in any case, involving the addition of catalyst to the mechanical stirred solution containing GPTMS and solvent. Before use, Mag-H⁺ was dried in an oven at 120 °C overnight. The polymerization reaction of GPTMS is described in Scheme 1.



Scheme 1. Polymerization reaction of GPTMS

2.4.2 Detailed example of synthesis

In a flask containing 2 mL of GPTMS (0.0084 mol) mixed with 5 mL of dichloromethane, we added an amount of 20% by weight of dried Mag-H⁺. The mixture was stirred for 8h at room temperature (20 °C). For completing the reaction a drop distilled water was added, then the mixture is filtered to remove the catalyst and precipitated in 50 ml of cold methanol (CH₃OH). The resulting polymer was extracted by filtration, washed for several times and dried in vacuum over night and weighed.

3. Results and Discussions

3.1 Characterization of Mag-H⁺

3.1.1 FT-IR Analysis

FT-IR spectrum of Mag-H⁺ compared to the raw-Maghnite Figure 1 shows that the hydrated structure of Maghnite-H⁺ results in characteristic vibrations of hydroxyl groups around 3400 cm⁻¹ and 3600 cm⁻¹. The intense band 1004 cm⁻¹ corresponds to the valence vibration of Si-O in the tetrahedral layer. Various other absorption bands at 780, 520, and 500 cm⁻¹ can be attributed to the montmorillonite clay structure. All these expected absorption bands confirm that the structure of the compound is thus in good agreement with vibration values obtained from the literature [38-40].

3.1.2 XRD Analysis

The X-ray diffractograms of the raw-Maghnite and the Mag-H⁺ are shown in Figure 2. The increase of interlayer distance *d* (001) = 11.20 Å in raw-Maghnite, characteristic of a single water layer between the sheets to a *d*(001) = 15 Å, distance attributed to two interlamellar water layer in Mag-H⁺. This increase indicates that there is a cationic exchange of the cation ions (Na⁺, Ca²⁺, K⁺, NH₄⁺, and Mg²⁺)

and a substitution of the H⁺ ions into the leaves of the montmorillonite [34-36].

3.2 Characterization of the Obtained Polymer (PGPTMS)

3.2.1 FTIR analysis

FTIR spectrum of GPTMS monomer and PGPTMS synthesized in solution using CH₂Cl₂ as solvent and in bulk are shown, respectively, in Figure 3 (a), Figure 3 (b) and Figure 3 (c). The characteristic absorption peaks of the epoxy group observed at around 778-815 cm⁻¹ and 900-910 cm⁻¹ [41] in the spectrum of the monomer Figure 3 (a) disappeared partially after polymerization of GPTMS in solution Figure 3 (b) and completely in bulk Figure 3 (c).

The FTIR spectrum of polymer PGPTMS synthesized in solution and in bulk was assigned as follows some references method [4-8,28,42]. Characteristic bands of GPTMS epoxy ring were located at: 500 cm⁻¹ (Si-O in Si-O-CH₃); 734 and 841 cm⁻¹ (C-C), 1089 cm⁻¹ (-CO in Si-O-CH₃); 1190 cm⁻¹ (-CO in C-O-C); 1016 cm⁻¹ (-CO epoxy ring); 1480 cm⁻¹ (-CH); 2800-3000 cm⁻¹ (-CH₂ and -CH₃) and 3360 cm⁻¹ (-OH). According to the literature, the peak lo-

cated at 907 cm⁻¹ could describe the elongation of C-O of C-OH end groups [42-45]. The absorption band around 1016 cm⁻¹, is also attributed to asymmetric stretching of Si-O-Si bonds [5] is observed in both polymerization. This bond is formed by the epoxy group reacting with water in air or adsorbed by Mag-H⁺ during the PGPTMS reprocessing procedure.

It is observed that there is an increment of the intensity of the absorption band corresponding to the group (C-O) at about 1017 cm⁻¹ for the PGPTMS prepared in bulk Figure 3(c) to that prepared in solution Figure 3(b), which indicates the formation of poly (ethylene oxide) in bulk with a degree of polymerization greater than that in solution. As well as, a large difference in the intensity and width of the absorption band of hydroxyl group presented at about 3360 cm⁻¹, this band is more intense and wider in spectrum (c) than that observed in spectrum (b).

3.2.2 ¹H-NMR analysis

The chemical displacement of the protons of the GPTMS and the PGPTMS are shown in Figure 5. Comparing the two spectra, it can be

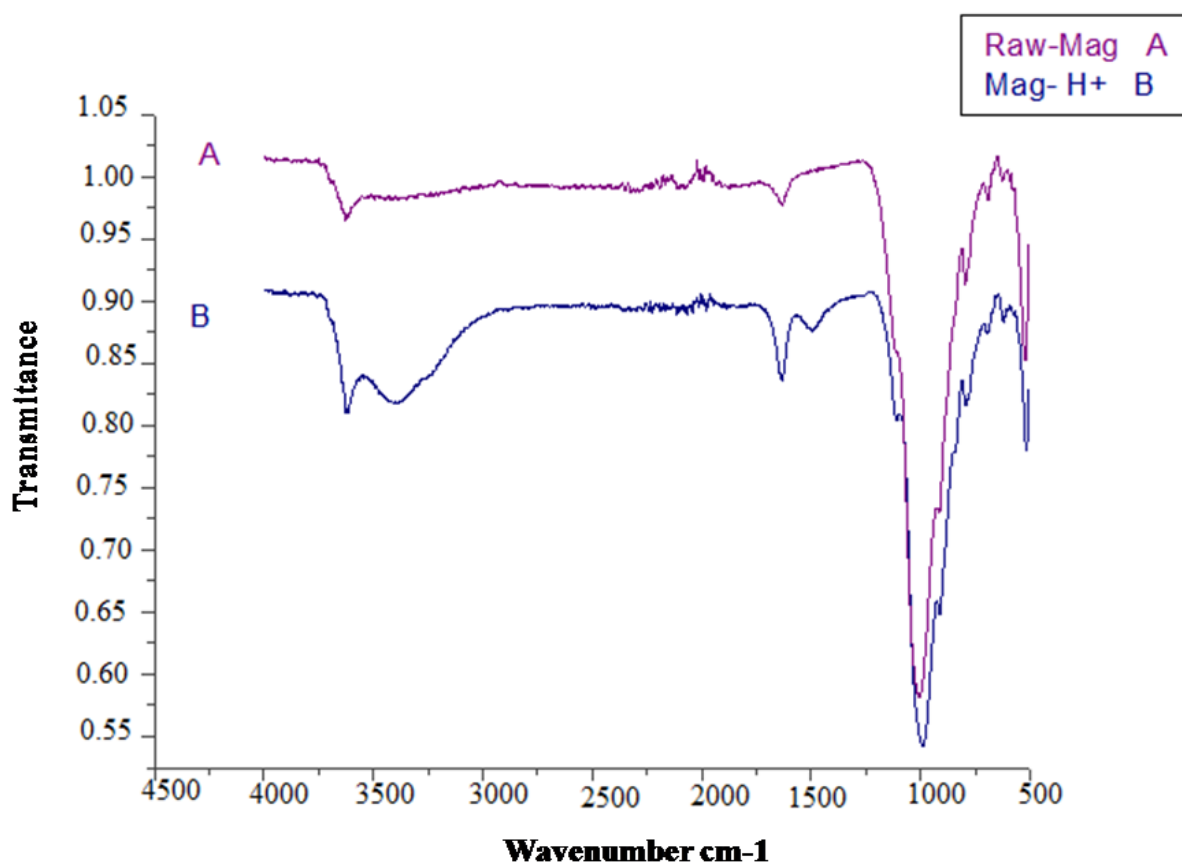


Figure 1. FTIR spectrum of Raw-Maghnite (A) and Mag-H+ 0.25 M (B).

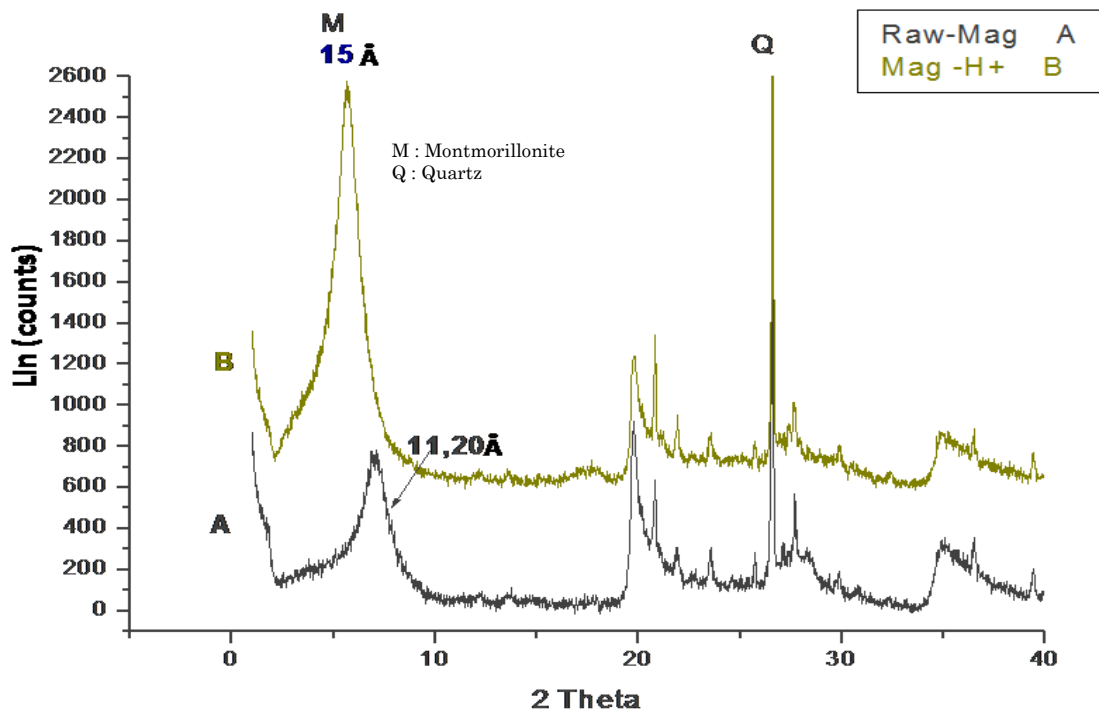


Figure 2. X-Ray diffractogram of Raw-Maghnite (A) and Mag-H+ 0.25 M (B).

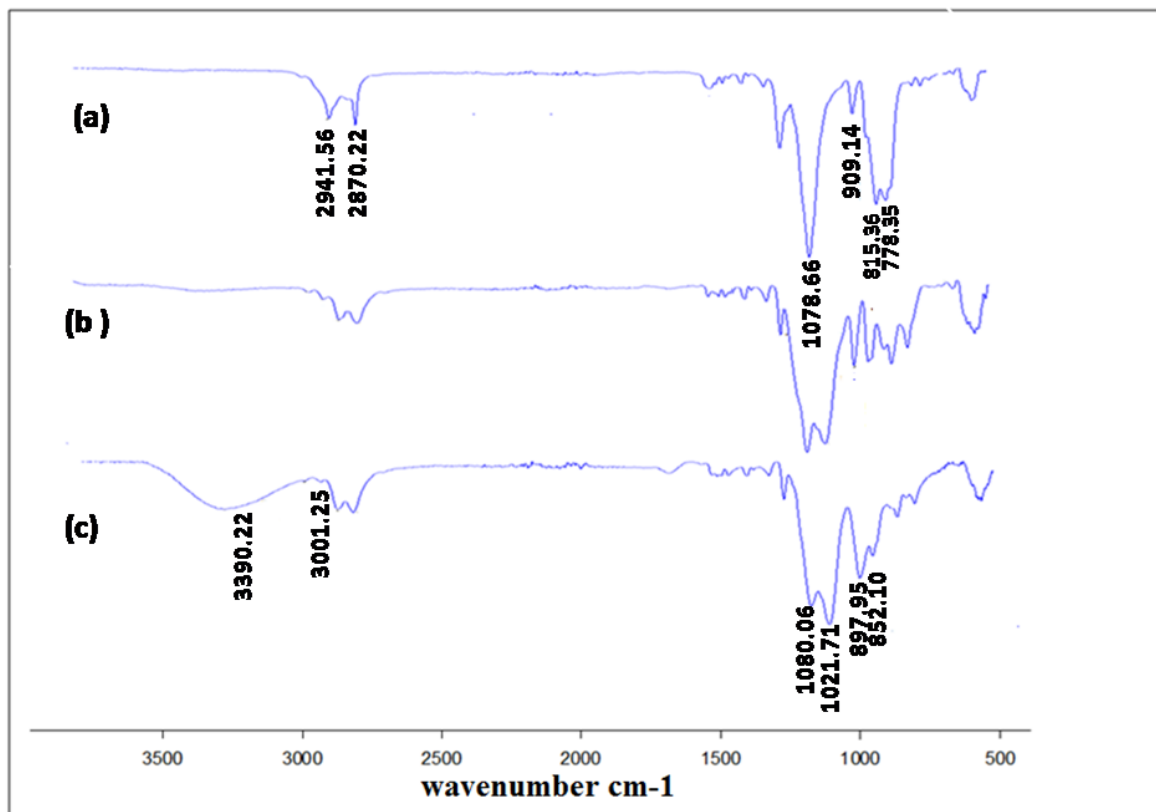


Figure 3. FTIR spectrums of GPTMS (a), the synthesized PGPTMS in solution (b) and in bulk (c).

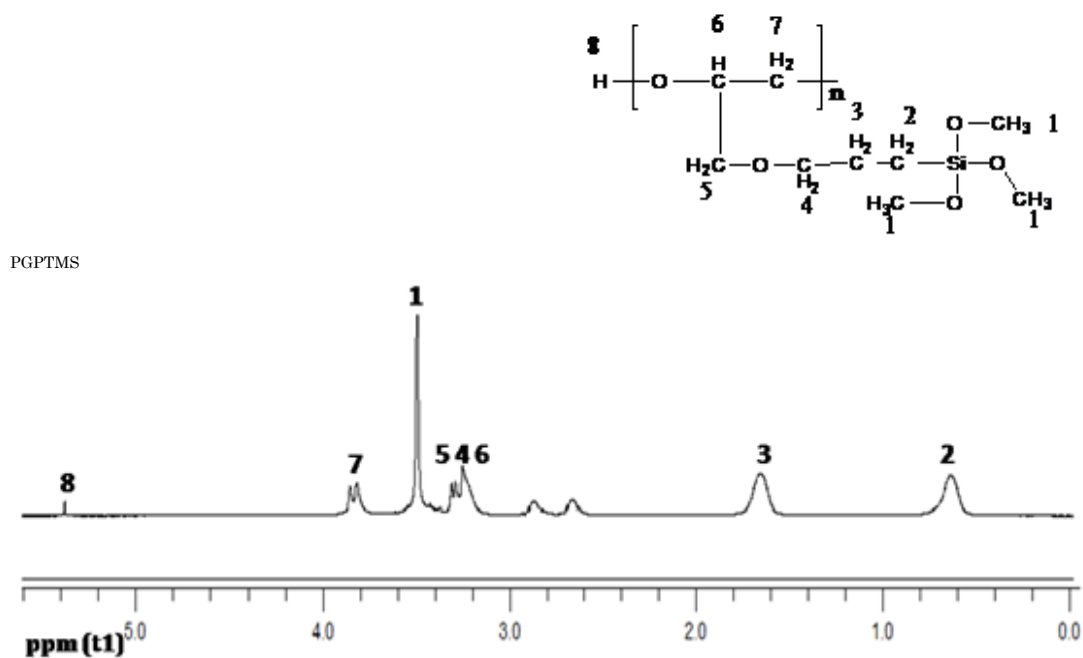
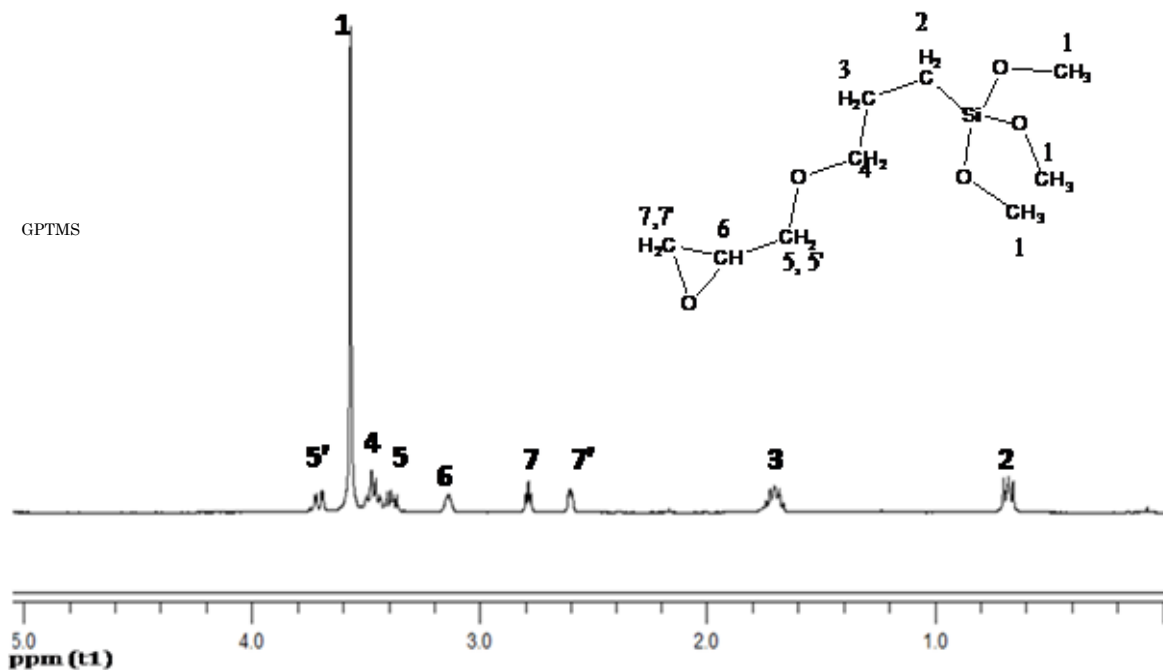


Figure 4. ^1H -NMR spectra of GPTMS and PGPTMS prepared in bulk at 0°C for 24 h.

seen that the change in chemical shift and coupling of the resonances of H6, H7, and H7' in the spectrum. We also see the appearance of a multiplets around 3.2 and 3.4 ppm corresponding to protons H4, H5, and H6 in PGPTMS polymer spectrum after ring-opening polymerization, which is in good agreement with literature data [5,7,28]. The signal at 3.48 ppm corresponds to the protons in the alkoxide group (Si-O-CH₃) in the two spectra confirms that only the ring opening polymerization is set up keeping the alkoxide function. The appearance of a peak at 5.4 ppm indicates the hydroxy end group O-H of polymer product due to the opening of the epoxide rings. The chemical shifts of the protons of the polymer synthesized are in agreement with those of the literature [4-8,28]. The results obtained by ¹H-NMR analysis show clearly the ring-opening polymerization of monomer, which are confirmed by the FTIR analysis.

3.2.3 ²⁹Si-MAS/NMR analysis

The ²⁹Si-MAS/NMR (²⁹Si-Magic angle spinning/nuclear magnetic resonance) spectrum of polymer PGPTMS shown in Figure 6 allows to

determine the alkoxysilane functions present in the hybrid polymer. It clearly shows the occurrence of hydrolysis by the presence of two major peaks, indicating the formation of two and three new siloxane bonds, respectively, from GPTMS [22,46]. The peaks at -58.30 and -66.66 ppm were observed for the corresponding absorption of monohydroxy-substituted silica of Figure 7 (RSi(OSi)₂(OH)) (T₂) and nonhydroxy-substituted silica (RSi(OSi)₃) (T₃). These groups might be produced by the epoxy group reacting with water in air or adsorbed by Mag-H⁺ during the PGPTMS reprocessing process.

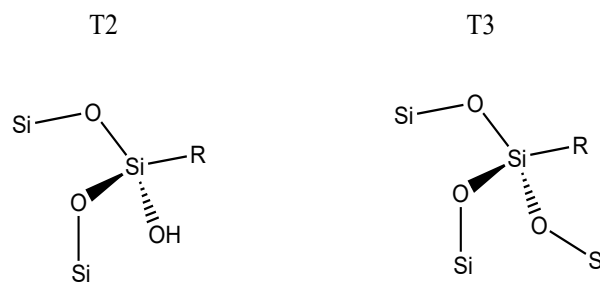


Figure 6. Species silicon atom types T2 et T3 represent in the organosilane.

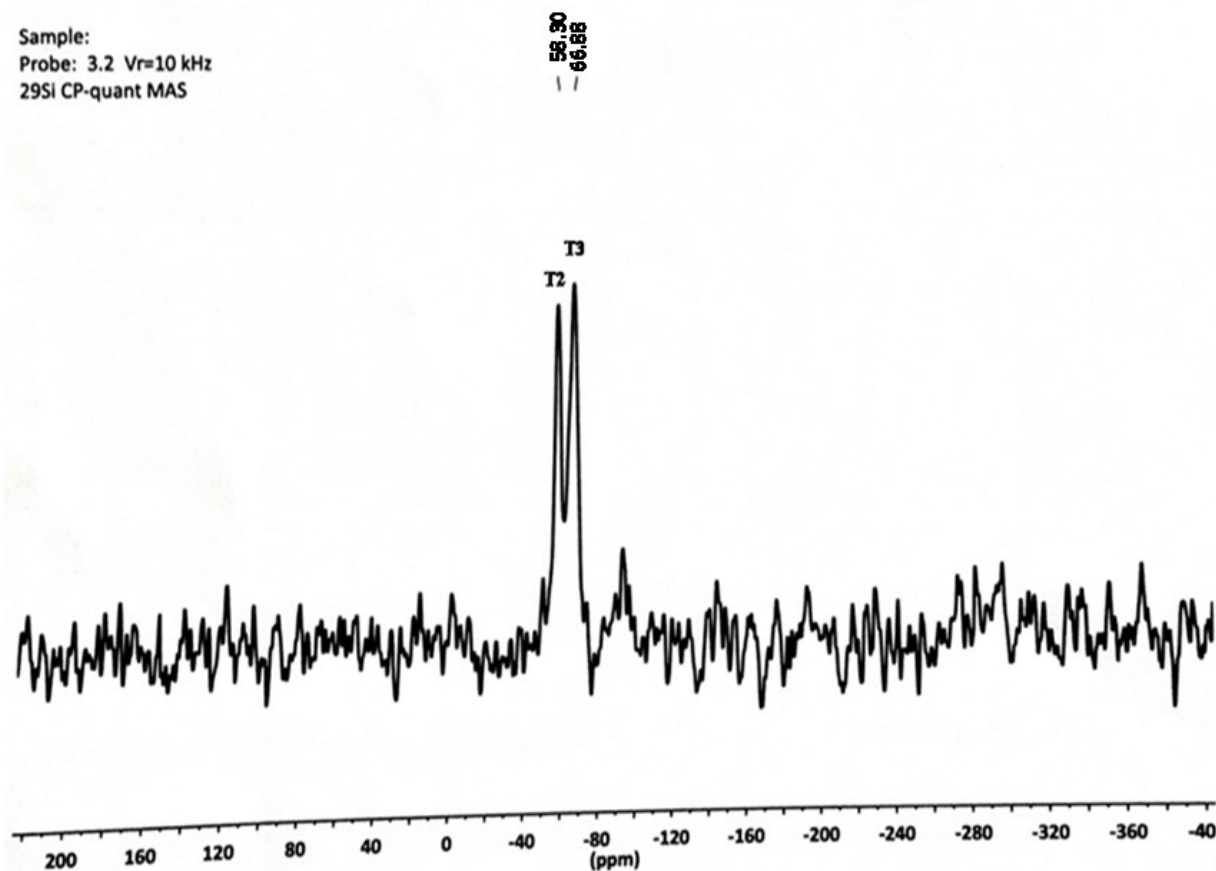


Figure 5. ²⁹Si-MAS/NMR spectrum of PGPTMS prepared in bulk at 0 °C for 24 h.

ture. The same results are obtained during the synthesis of epoxy-silica hybrid resins [47,48]. Therefore, the ^{29}Si -NMR results confirmed the conclusions drawn from the FT-IR analysis.

3.2.4 Thermogravimetry (TGA) analysis

In order to follow the thermal stability of the obtained product, the thermogravimetric analysis is used. The thermogravimetric curve Figure 7 represents the relative mass loss as a function of the heating temperature of PGPTMS compared with the GPTMS, hence depicting that the PGPTMS is thermally stable [28] with a degradation start temperature greater than 300 °C. The degradation rate of polymer increased with increasing temperature and reached its maximum at 370.5 °C, then is gradually decreased.

It also shows that the curve is consisted of a single distinct part associated with a single loss of mass indicating that the obtained product consist of a single type of polymer and not a mixture. Also it shows that this polymer does not keep any trace of solvent or starting materials (monomer) knowing that the boiling point of the monomer used (3-glycidoxypropyltrimethoxysilane) is 120 °C and that the evaporation temperature of the solvent of the reaction (dichloromethane) is 40 °C. These two temperatures differ from those indicated on the

curve confirming the formation of new product which is more stable than the monomers.

3.2.5 Differential Scanning Calorimetry DSC

Figure 8 shows the DSC curve of PGPTMS in bulk, the glass-transition temperatures T_g of PGPTMS is below -30 °C (-31.27 °C). This result is in accordance with previous literature

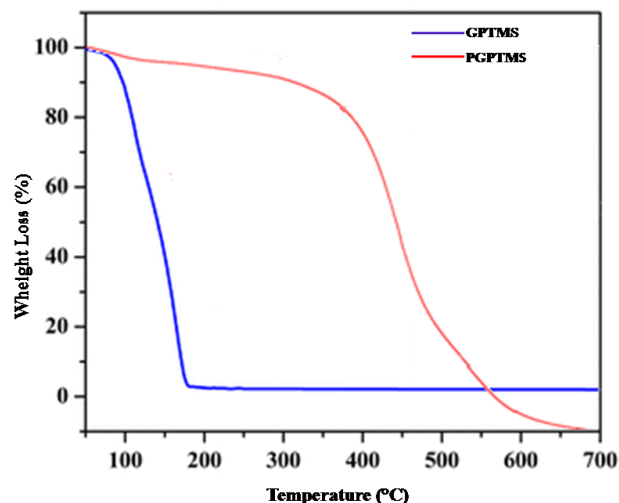


Figure 7. Thermogravimetric curves of GPTMS and PGPTMS prepared in bulk at 25 °C for 24 h.

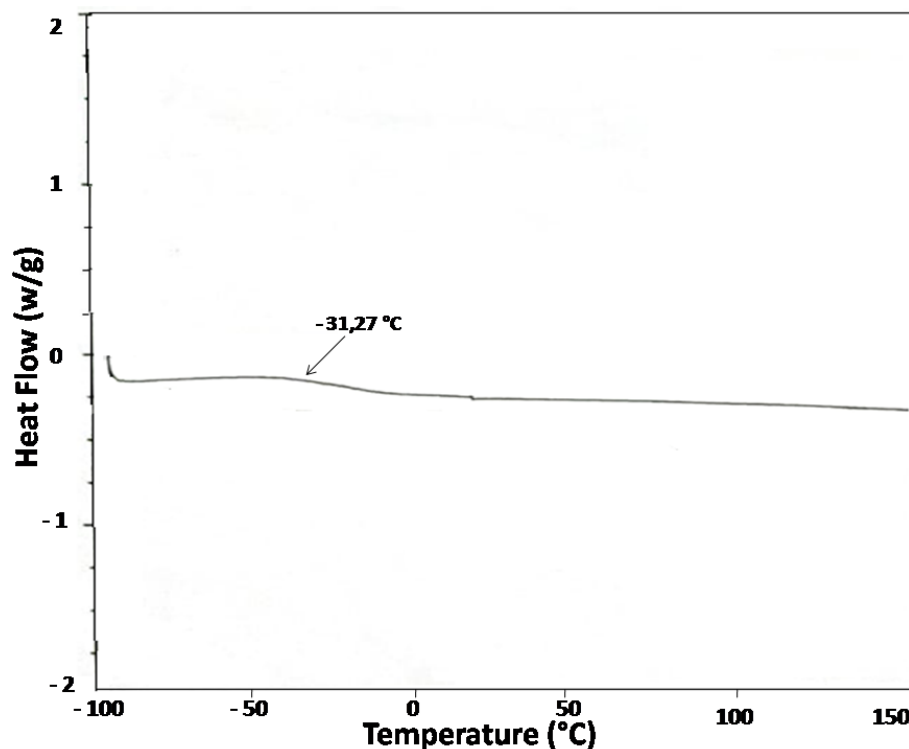


Figure 8. DSC curve of PGPTMS in bulk.

[28]. The low T_g indicates the good resistance of the polymer at low temperature.

3.3 Kinetic Study of the Ring-opening Polymerization of GPTMS Catalyzed by Mag-H⁺

The change in the reaction conditions of the PGPTMS synthesis reaction makes it possible to carry out a kinetic study on the ring-opening of the epoxide and the evolution of the PGPTMS yield. In order to find the optimum conditions of the polymerization of GPTMS, we studied the effect of different parameters and their influence on the yield of the obtained polymers, such as: the effect of catalyst amount, temperature and reaction time. Preliminary experiments were carried out with varied temperature, catalyst amount and reaction time (Figures 11, 12, and 13).

3.3.1 Effect of Mag-H⁺ amount on the yield of PGPTMS

The polymerization is carried out at 20 °C for 8 h in bulk and in solution (5 mL of CH₂Cl₂), using various amounts of Mag-H⁺ (5, 10, 15, 20, and 25 wt%). For the obtained polymers in bulk, the results of the FTIR analysis in the Figure 9 show that the opening of the epoxy ring starts from the addition of 15% by weight of the catalyst Figure 9 (b) and continues with the increase of the amount of Mag-H⁺. This is indicated by the decrease of the intensity of the characteristic absorption peak of the epoxy group observed at around 910 cm⁻¹ in the spectrum of monomer Figure 9 (a) and it's disappeared completely after polymerization of GPTMS Figure 9 (e), and the intensity of C-O-C bond becomes more intense by the increasing of the catalyst amount due to the formation of polymer chain. Also, it is observed the widen-

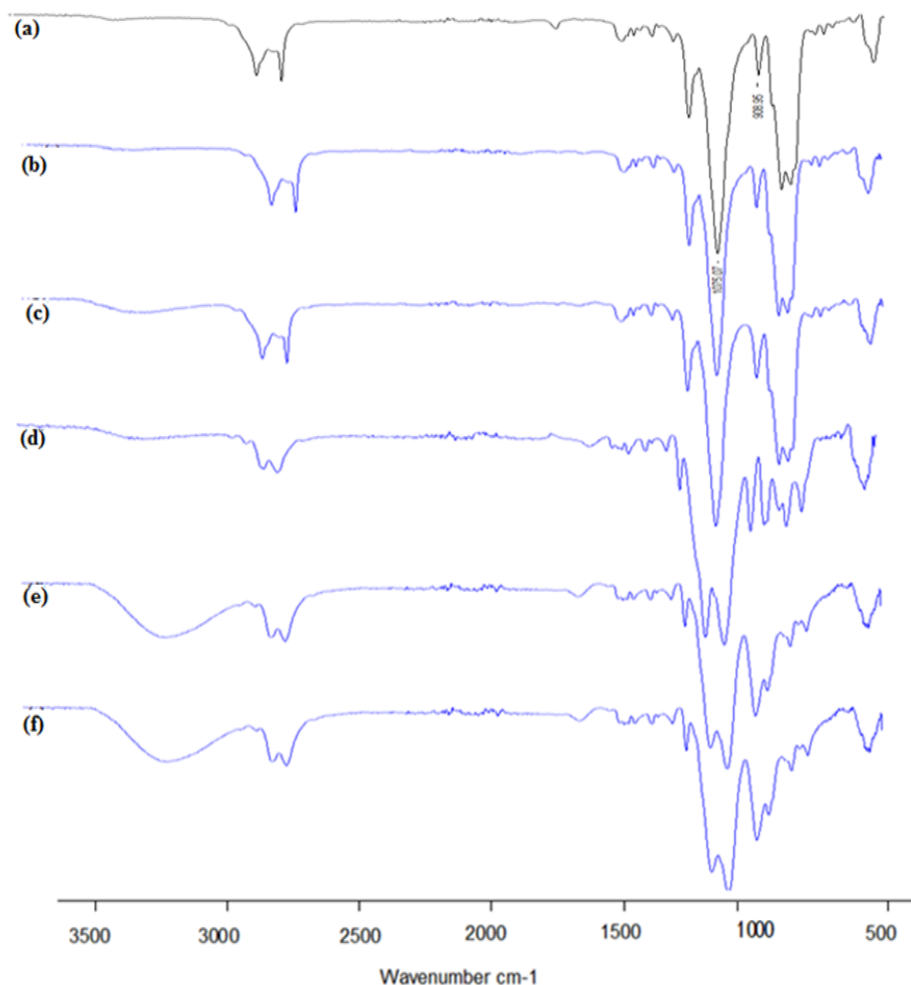


Figure 9. FTIR spectrum of GPTMS (a), PGPTMS using amounts of Mag-H⁺ (5; 10; 15; 20; and 25 wt%) (b, c, d, e, and f) respectively, in bulk at 20 °C for 8 h.

ing of the hydroxy end group O-H band at around 3450 cm^{-1} of Figure 9 (e) and (f) which is more formed by the increasing of the ring opening. As is shown in the Figure 10, the yield of polymer increased with the amount of Mag-H⁺ for both polymerization, in solution and in bulk. It reaches its maximum at 20% by weight of Mag-H⁺ for polymers prepared in bulk, beyond this value the yield decreases. The obtained results show the effect of Mag-H⁺ as a cationic catalyst, the increase of amount of catalyst increase the active sites responsible for the initiation and acceleration of the polymerization reaction. This is indicated by the higher viscosity of the environment in bulk polymerization of GPTMS giving best yield compared to those obtained for GPTMS polymerized in solu-

tion. Similar results are obtained by other authors [32-34,37]. As is shown in the Figure 10, the yield of polymer increased with the amount of Mag-H⁺ for both polymerization, in solution and in bulk. It reaches its maximum at 20% by weight of Mag-H⁺ for polymers prepared in bulk, beyond this value the yield decreases. The obtained results show the effect of Mag-H⁺ as a cationic catalyst, the increase of active sites available in catalyst responsible for the initiation and acceleration of the polymerization reaction until the saturation of these sites. This is indicated by the higher viscosity of the environment in bulk polymerization of GPTMS giving best yield compared to those of GPTMS polymerized in solution. Similar results were obtained by other authors [32-34,37].

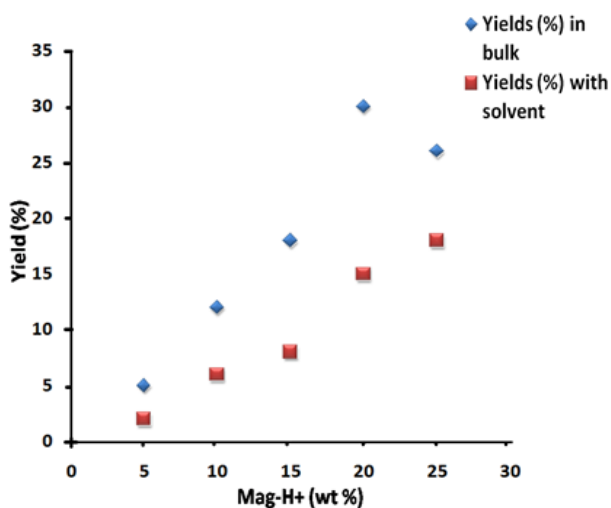


Figure 10. The effect of Mag-H⁺ amount on the PGPTMS yield (in bulk and in solution) at 20 ± 2 °C for 8 h.

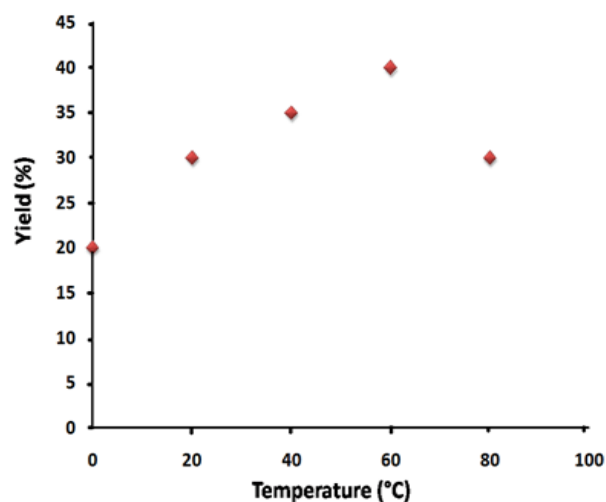


Figure 11. The effect of temperature on the PGPTMS yield, in bulk with 20% wt of Mag-H⁺ for 8 h.

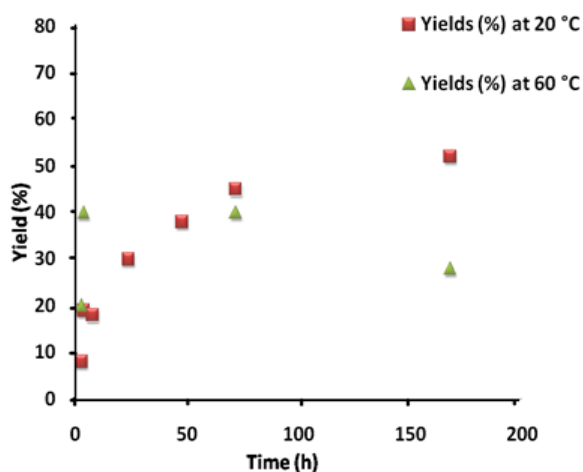


Figure 12. Effect of the time on the yield of PGPTMS in bulk, with 20 wt% of Mag-H⁺ at 20 °C and 60 °C for 8 h.

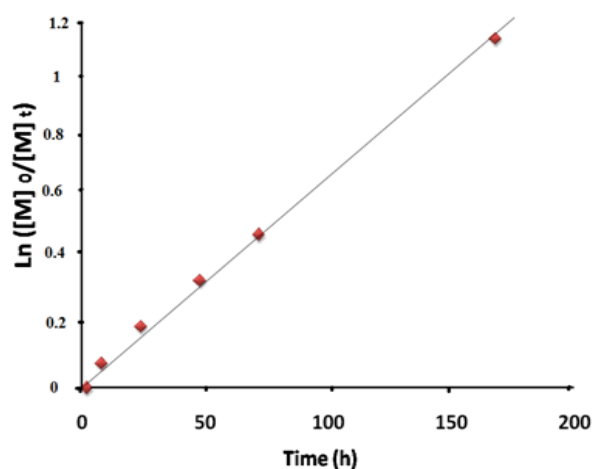


Figure 13. $\ln ([M]_0/[M]_t)$ as a function of time for $T = 20$ °C in bulk, conditions; $[M]_0 = 0.0084$ mol/L for Mag-H⁺/GPTMS = 20 wt%.

3.3.2 Effect of the temperature on the yield of PGPTMS

Figure 11 shows the effect of temperature on the yield of the ring-opening polymerization of GPTMS. This study is carried out in bulk at different temperatures: 0, 20, 40, 60, 80, 100, and 120 °C for 8 h with 20% by weight of Mag-H⁺. The yield of the obtained product evolves relatively with the increase of the temperature and reaches maximum 40% at 60 °C; at this temperature (optimal point) a transparent polymer with better performance was formed. The yield decreases at 80 °C and it is also shown that at high temperature, the appearance of the polymer is changed and the color becomes light brown. For both temperatures 100 and 120 °C, the product obtained is an insoluble composite (clay/polymer). It is noted that the temperature has a great influence on the yield and the product appearance.

3.3.3 Effect of the time on the yield of PGPTMS

As seen in Figure 12, after three hours of polymerization in bulk, the conversion rises up dramatically and increases in presence of 20 wt% of Mag-H⁺ at both temperatures 20 and 60 °C. It can be explained by the heterogeneous reaction which requires an adsorption process before monomer reaction with the acidic active site located in the Maghnite and being initiated, after a period of continuous stirring, the monomer started to contact with the acidic sites and polymerization took place. The Figure 12 shows that at the end of polymerization time 8 h, the best yields reaches (40% at 60 °C and 30% at 20 °C). It is possible to conclude that the ring-opening of the epoxide is initiated from 8 h of stirring, using 20 wt% of Mag-H⁺. After this time, the yield increases until reaching 68% after 7 days of stirring at room temperature (20 °C). In contrast to high temperature (60 °C), we recorded a remarkable decrease in performance beyond 24 hours (28%).

Figure 13 shows that the polymerization is first order with respect to monomer. The polymerization of GPTMS initiated by Mag-H⁺ can be described by the following formula:

$$vp = -\frac{d[M]}{dt} = kp[M] \quad (1)$$

where k_p is the polymerization rate constant. At 20 °C, value of k_p is $1.53 \times 10^{-6} \text{ s}^{-1}$.

4. Conclusion

PGPTMS were synthesized successfully under mild conditions, using Mag-H⁺ as an ecological acidic catalyst for ring-opening polymerization of GPTMS, in bulk and in solution. The polymerization proceeds via a cationic mechanism due to the presence of intercalated protons in the lamellar structure of Maghnite. However, bulk polymerization remains a preferred technique for PGPTMS synthesis to be consistent with the principles of green chemistry. The optimum reaction conditions were defined by studying the effect of different parameters and their influence on the yield of the obtained polymers. The higher viscosity of the environment in bulk polymerization PGPTMS giving best yields compared to those of GPTMS polymerized in solution. The temperature and the polymerization time have a great influence on the yield and the product appearance. The structure of the obtained polymer has been perfectly confirmed by FTIR, ¹H NMR and ²⁹Si-NMR. The thermal properties have been given by TGA and DSC analysis. The good properties catalytic of the green catalyst (Mag-H⁺) and the simplicity of the method for the synthesis of PGPTMS without requiring very low or very high temperature nor high pressures, are less expensive and environmentally friendly. These make it an attractive method for the green synthesis of PGPTMS and their derivatives.

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References

- [1] Li, L., He, B., Chen, X. (2007). Epoxysilane crosslinking of rigid poly (vinyl chloride). *Journal of Applied Polymer Science*, 106, 3610-3616. doi: 10.1002/app.26890.
- [2] Tian, M., Liang, W., Rao, G., Zhang, L., Guo, C. (2005). Surface modification of fibrillar silicate and its reinforcing mechanism on FS/rubber composites. *Composites Science and Technology*, 65, 1129-1138. doi: 10.1016/j.compscitech.2004.11.008
- [3] Zhang, H.J., Zhang, Z.Z., Guo, F., Liu, W.M. (2009). Friction and wear behavior of the hybrid PTFE/cotton fabric composites filled with TiO₂ nanoparticles and modified TiO₂ nanoparticles. *Polymer Engineering & Science*, 49, 115-122. doi: 10.1002/pen.21228

- [4] Gabrielli, L., Russo, L., Poveda, A., Jones, J.R., Nicotra, F., Jiménez-Barbero, J. and Cipolla, L. (2013), Epoxide Opening versus Silica Condensation during Sol–Gel Hybrid Biomaterial Synthesis. *Chem. Eur. J.*, 19, 7856-7864. doi: 10.1002/chem.201204326
- [5] Innocenzi, P., Brusatin, G., Babonneau, F. (2000). Competitive polymerization between organic and inorganic networks in hybrid materials. *Chemistry of Materials*, 12, 3726-3732. doi: 10.1021/cm001139b
- [6] Innocenzi, P., Brusatin, G., Guglielmi, M., Bertani, R. (1999). New Synthetic Route to (3-Glycidoxypropyl) trimethoxysilane-Based Hybrid Organic – Inorganic Materials. *Chemistry of Materials*, 11, 1672-1679. doi: 10.1021/cm980734z
- [7] Innocenzi, P., Esposto, M., Maddalena, A. (2001). Mechanical properties of 3-glycidoxypropyltrimethoxysilane based hybrid organic-inorganic materials. *Journal of Sol-Gel Science and Technology*, 20, 293-301. doi: 10.1023/A:1008782203971
- [8] Innocenzi, P., Sassi, A., Brusatin, G., Guglielmi, M., Favretto, D., Bertani, R., Babonneau, F. (2001). A Novel Synthesis of Sol–Gel Hybrid Materials by a Nonhydrolytic/Hydrolytic Reaction of (3-Glycidoxypropyl) trimethoxysilane with $TiCl_4$. *Chemistry of Materials*, 13, 3635-3643. doi: 10.1021/cm011034o
- [9] Laine, R.M. (2012). Inorganic and organometallic polymers with special properties. *Springer Science & Business Media*.
- [10] Sforca, M., Yoshida, I., Nunes, S. (1999). Organic–inorganic membranes prepared from polyether diamine and epoxy silane. *Journal of Membrane Science*, 159, 197-207. doi: 10.1016/S0376-7388(99)00059-9
- [11] Sorek, Y., Zevin, M., Reisfeld, R., Hurvits, T., Ruschin, S. (1997). Zirconia and Zirconia–ORMOSIL Planar Waveguides Prepared at Room Temperature. *Chemistry of Materials*, 9, 670-676. doi: 10.1021/cm960135x
- [12] Innocenzi, P., Martucci, A., Guglielmi, M., Armelao, L., Pelli, S., Righini, G., Battaglin, G. (1999). Optical and surface properties of inorganic and hybrid organic–inorganic silica–titania sol–gel planar waveguides. *Journal of Non-Crystalline Solids*, 259, 182-190. doi: 10.1016/S0022-3093(99)00534-7
- [13] Brusatin, G., Innocenzi, P., Guglielmi, M., Bozio, R., Meneghetti, M., Signorini, R., Prato, M. (1999). 3-(glycidoxypropyl)-trimethoxysilane-based matrices tailored for optical limiting applications. Materials and Devices for Photonic Circuits. *International Society for Optics and Photonics*, 3803, 90-97. doi: 10.1117/12.366748.
- [14] Innocenzi, P., Brusatin, G., Guglielmi, M., Signorini, R., Bozio, R., Maggini, M. (2000). 3-(Glycidoxypropyl)-trimethoxysilane– TiO_2 hybrid organic–inorganic materials for optical limiting. *Journal of Non-Crystalline Solids*, 265, 68-74. doi: 10.1016/S0022-3093(99)00898-4
- [15] Innocenzi, P., Brusatin, G., Guglielmi, M., Signorini, R., Meneghetti, M., Bozio, R., Prato, M. (2000). Optical limiting devices based on C60 derivatives in sol-gel hybrid organic-inorganic materials. *Journal of Sol-Gel Science and Technology*, 19, 263-266. doi: 10.1023/A:1008704825802
- [16] Signorini, R., Meneghetti, M., Bozio, R., Maggini, M., Scorrano, G., Prato, M., Guglielmi, M. (2000). Optical limiting and non linear optical properties of fullerene derivatives embedded in hybrid sol–gel glasses. *Carbon*, 38, 1653-1662. doi: 10.1016/S0008-6223(00)00055-5
- [17] Casalboni, M., De Matteis, F., Proposito, P., Pizzoferrato, R. (1999). Optical investigation of infrared dyes in hybrid thin films. *Applied Physics Letters*, 75, 2172-2174. doi: 10.1063/1.124955
- [18] Pomogailo, A. (2005). Polymer sol-gel synthesis of hybrid nanocomposites. *Colloid Journal*, 67, 658-677. doi: 10.1007/s10595-005-0148-7
- [19] Schmidt, H. (1985). New type of non-crystalline solids between inorganic and organic materials. *Journal of Non-Crystalline Solids*, 73, 681-691. doi: 10.1016/0022-3093(85)90388-6
- [20] Schmidt, H. (1994). Multifunctional inorganic-organic composite sol-gel coatings for glass surfaces. *Journal of Non-Crystalline Solids*, 178, 302-312. doi: 10.1016/0022-3093(94)90299-2
- [21] Popall, M., Durand, H. (1992). Inorganic–organic copolymers as solid state Li^+ electrolytes. *Electrochimica Acta*, 37, 1593-1597. doi: 10.1016/0013-4686(92)80118-6
- [22] Riegel, B., Blittersdorf, S., Kiefer, W., Hofacker, S., Müller, M., Schottner, G. (1998). Kinetic investigations of hydrolysis and condensation of the glycidoxypropyltrimethoxysilane/aminopropyltriethoxy-silane system by means of FT-Raman spectroscopy I. *Journal of Non-Crystalline Solids*, 226, 76-84. doi: 10.1016/S0022-3093(97)00487-0
- [23] Sanchez, C., Ribot, F., Lebeau, B. (1999). Molecular design of hybrid organic-inorganic nanocomposites synthesized via sol-gel chemistry. *Journal of Materials Chemistry*, 9, 35-44. doi: 10.1039/A805538F

- [24] Šapić, I.M., Bistričić, L., Volovšek, V., Dananić, V. (2014). Vibrational Analysis of 3-glycidoxypropyltrimethoxysilane polymer. *Macromolecular Symposia. Wiley Online Library*, 339, 122-129. doi: 10.1002/masy.201300145
- [25] Allothman, Z.A., Apblett, A.W. (2009). Preparation of mesoporous silica with grafted chelating agents for uptake of metal ions. *Chemical Engineering Journal*, 155, 916-924. doi: 10.1016/j.cej.2009.09.028
- [26] Lin, S., Yao, G., Qi, D., Li, Y., Deng, C., Yang, P., Zhang, X. (2008). Fast and efficient proteolysis by microwave-assisted protein digestion using trypsin-immobilized magnetic silica microspheres. *Analytical Chemistry*, 80, 3655-3665. doi: 10.1021/ac800023r
- [27] Xi, H., Li, Z., Liang, Z. (2000). Synthesis of New Organic/Inorganic Hybrid Material Containing 4-Nitro-4-amino Azobenzene and Its Second-Order Nonlinear Optical Properties. *Acta Polymerica Sinica*, 6, 757-762.
- [28] Wang, J., Fan, X., Tian, W., Wang, Y., Li, J. (2011). Ring-opening polymerization of γ -glycidoxypropyltrimethoxysilane catalyzed by multi-metal cyanide catalyst. *Journal of Polymer Research*, 18, 2133-2139. doi: 10.1007/s10965-011-9623-5.
- [29] Buyl, F.D., Kretschmer, A. (2008). Understanding hydrolysis and condensation kinetics of γ -glycidoxypropyltrimethoxysilane. *The Journal of Adhesion*, 84(2), 125-142. doi: 10.1080/00218460801952809.
- [30] Harrane, A., Meghabar, R., Belbachir, M. (2002). A protons exchanged montmorillonite clay as an efficient catalyst for the reaction of isobutylene polymerization. *International Journal of Molecular Sciences*, 3, 790-800. doi: 10.3390/i3070790
- [31] Belbachir, M., Bensaoula, A. (2001). Composition and method for catalysis using bentonites. *US Patent 6. 274, 527 B1*.
- [32] Belbachir, M., Bensaoula, A. (2003). Composition and method for catalysis using bentonites. *US Patent. 0069446 A1*,
- [33] Beloufa, K., Sahli, N., Belbachir, M. (2010). Synthesis of copolymer from 1,3,5-trioxane and 1,3-dioxolane catalyzed by Maghnite-H⁺. *Journal of Applied Polymer Science*, 115, 2820-2827. doi: 10.1002/app.30901
- [34] Bennabi, S., Sahli, N., Belbachir, M., Brachais, C.-H., Boni, G., Couvercelle, J.-P. (2017). New approach for synthesis of poly(ethylglyoxylate) using Mag-H⁺, an Algerian proton exchanged montmorillonite clay, as an eco-catalyst. *Journal of Macromolecular Science, Part A*, 54, 843-852. doi: 10.1080/10601325.2017.1339558
- [35] Derdar, H., Belbachir, M., Harrane, A. (2019). A Green Synthesis of Polylimonene Using Mag-H⁺, an Exchanged Montmorillonite Clay, as Eco-Catalyst. *Bulletin of Chemical Reaction Engineering & Catalysis*, 14, 69-78. doi: 10.9767/bcrec.14.1.2692.69-78
- [36] Reguieg, F., Sahli, N., Belbachir, M. (2015). Nanocomposite hydrogels based on water soluble polymer and montmorillonite-Na⁺. *Oriental Journal of Chemistry*, 31, 1645-1657. doi: 10.13005/ojc/310343
- [37] Reguieg, F., Sahli, N., Belbachir, M., Lutz, P.J. (2006). One-step synthesis of bis-macromonomers of poly(1,3-dioxolane) catalyzed by Maghnite-H⁺. *Journal of Applied Polymer Science*, 99, 3147-3152. doi: 10.1002/app.22935
- [38] Breen, C., Madejová, J., Komadel, P. (1995). Characterisation of moderately acid-treated, size-fractionated montmorillonites using IR and MAS NMR spectroscopy and thermal analysis. *Journal of Materials Chemistry*, 5, 469-474. doi: 10.1039/JM9950500469
- [39] Čičel, B., Komadel, P., Bednáriková, E., Madejová, J. (1992). Mineralogical composition and distribution of Si, Al, Fe, Mg and Ca in the fine fractions of some Czech and Slovak bentonites. *Geologica Carpathica, Series Clays*, 43, 3-7.
- [40] Farmer, V.C. (1974). Infrared spectra of minerals. *Mineralogical society*. P. 133
- [41] Grasselli, J.G., Ritchey, W.M. (1973). CRC atlas of spectral data and physical constants for organic compounds. OH : *CRC press Cleveland*.
- [42] Fontinha, I.R., Salta, M.M., Zheludkevich, M.L., Ferreira, M.G. (2013). EIS study of amine cured epoxy-silica-zirconia sol-gel coatings for corrosion protection of the aluminium alloy EN AW 6063. *Portugaliae Electrochimica Acta*, 31, 307-319. doi: 10.4152/pea.201306307
- [43] Colthup, N., Daly, L.H., Wiberley, S.E. (1964). Introduction to Infrared and Raman Spectroscopy, *Academic Press Inc*, New York N Y.: 306-307.
- [44] Colthup, N., Daly, L., Wiberley, S.E. (1990). Introduction to Infrared and Raman Spectroscopy. *Academic Press*, New York.
- [45] de Luca, M.A., Martinelli, M., Barbieri, C.C. (2009). Hybrid films synthesised from epoxidised castor oil, γ -glycidoxy propyltrimethoxysilane and tetraethoxysilane. *Progress in Organic Coatings*, 65, 375-380. doi: 10.1016/j.porgcoat.2009.03.002

- [46] Templin, M., Wiesner, U., Spiess, H.W. (1997). Multinuclear solid-state-NMR studies of hybrid organic-inorganic materials. *Advanced Materials*, 9, 814-817. doi: 10.1002/adma.19970091011
- [47] Genet, C., Menu, M.-J., Gavard, O., Ansart, F., Gressier, M., Montpellaz, R. (2018). Innovative Formulation Combining Al, Zr and Si Precursors to Obtain Anticorrosion Hybrid Sol-Gel Coating. *Molecules*, 23, 1135. doi: 10.3390/molecules23051135
- [48] Liu, Y.L., Wu, C.S., Chiu, Y.S., Ho, W.H. (2003). Preparation, thermal properties, and flame retardance of epoxy-silica hybrid resins. *Journal of Polymer Science Part A: Polymer Chemistry*, 41, 2354-2367. doi: 10.1002/pola.10778