

# Catalytic Activity of Maghnite-H<sup>+</sup> in the Synthesis of Polyphenylmethylsiloxane under Mild and Solvent-free Conditions

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## Abstract

In this study, a new and easy strategy was discussed for the purpose of synthesizing of a polymer of phenylmethylcyclorosiloxane type (PPMS). The cationic ring opening polymerization of triphenyltrimethylcyclotrisiloxane ( $D_3^{Ph,Me}$ ) was initiated by a solid, efficient and environmentally-friendly catalyst called Maghnite-H<sup>+</sup>. Maghnite-H<sup>+</sup> is a natural clay composed essentially of montmorillonite, it is activated with an acid treatment by replacing the interlayer ions by protons, that results to the increase of the basal space, this may be confirmed by XRD analysis. The reaction was carried out without solvent at different temperatures and for different periods of time, using also several catalyst contents. Subsequently, the operating conditions were opted in order to obtain a maximum yield of the linear polymer and a high average molecular mass as well. The structure of polymers obtained was confirmed by IR analysis. <sup>1</sup>H NMR and <sup>13</sup>C NMR analyzes were used to follow the crosslinking of polymer chains over time. The thermal behavior was investigated by DSC analysis. The average molecular mass and the polydispersity indices were determined by GPC.

## Keywords

maghnite, catalyst, ring opening polymerization, ecological, polyphenylmethylcyclorosiloxane

## 1 Introduction

The manufacture of more than 80% of chemicals depends on catalytic reactions. To create new products, or to use new raw materials, chemists must therefore develop new catalysts. In particular, one of the current challenges for chemistry is to replace the hazardous catalysts, strong acids and bases with various mineral or biomass compounds [1]. Clay minerals possess various properties have led to their use by chemists for a wide variety of applications, for example as a texture agent in paints, bleaching agent for paper, or a reinforcing agent for polymer-based plastics, they are also used in heterogeneous catalysis to initiate several chemical reactions. The heterogeneous catalysis makes it possible to demonstrate the reduction of the number of steps and the economy of atoms. In addition, it deals in the course of development, the stakes of enantioselective catalysis, in particular compared to the criteria of green chemistry [2,3].

The objective of this work is based on heterogeneous catalysis using Maghnite, which makes it possible to carry out chemical reactions in order to synthesize silicone polymers at low temperature and in limited time. Maghnite is a natural Algerian clay obtained from the region of Maghnia that is located in the northwest of Algeria [4,5]. It is a new catalyst based on montmorillonite when activated with a strong acid. This catalyst was developed in Polymer Chemistry Laboratory «LCP», it has shown remarkable catalytic capabilities in polymerization reactions of various vinyl and heterocyclic monomers. Several studies have been carried out at the LCP concerning the introduction of Maghnite-H<sup>+</sup> in the initiation of polymerization reactions [6-8]. In other works, Maghnite has been used as an inorganic reinforcement and as an initiator at the same time in different reactions in order to synthesize nanocomposite materials [9-11]. In this case, we will study the possibility of using Maghnite-H<sup>+</sup> as a catalyst to obtain a new class of widely used polymers which are silicones.

The name silicone was given for the first time by Kipping in 1901 to describe compounds consisting of a sequence of silicon-oxygen units and organic side groups bound to the silicon atom (Scheme 1a). The most common example is

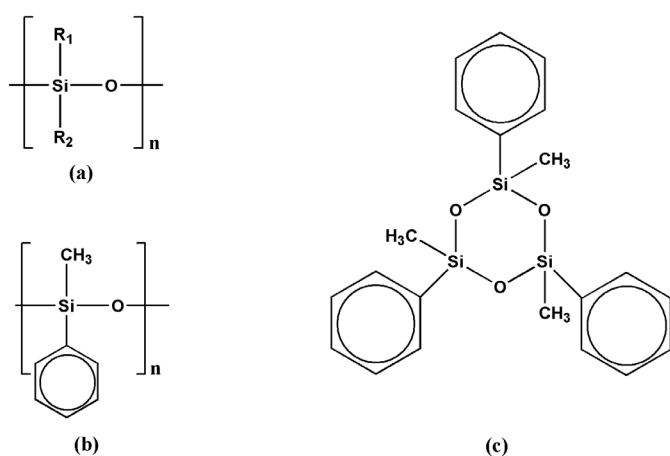
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polydimethylsiloxane [12,13]. Polydimethylsiloxane (PDMS) is the most commercially available siloxane polymer in the world. Despite the good characteristics of this material, such as high flexibility at low temperature, very high radiation resistance, higher thermal stability and refraction, some gaps persist [14,15]. Very often, these characteristics can be improved by the substitution of dimethylsiloxane units with those of phenylmethylsiloxane in the PDMS chain (Scheme 1b) [16,17]. The production of polyphenylmethylsiloxanes is usually carried out by anionic or cationic ring opening polymerization of triphenyltrimethylcyclotrisiloxane (Scheme 1c) [18-21]. They were obtained previously in the presence of strong bases as phosphazenebases [22-25], strong acids as dodecylbenzenesulfonic acid [26], triflic acid [27], tris(pentafluorophenyl)borane [28] and trifluoromethanesulfonic acid [29], etc.



**Scheme 1** The structure of (a) Silicone; (b) Polyphenylmethylsiloxane and (c)  $D_3^{\text{Ph,Me}}$

## 2 Experimental

### 2.1 Materials

Triphenyltrimethylcyclotrisiloxane ( $D_3^{\text{Ph,Me}}$ , 99%) was used as purchased from Aldrich chemical, without further purification. Methanol was purified by vacuum distillation. All other products have been used as received. Maghnite was obtained from Algerian company of bentonite (BENTAL), without any pretreatment.

### 2.2 Preparation of Maghnite- $H^+$

A mass of 30 g of raw Maghnite is combined with 120 ml of distilled water at room temperature, the suspension is left under stirring. After 30 min, 100 ml of a solution of sulfuric acid (0.23 M) is added, the stirring is continued for 48 h. After filtration and subsequent washing, the activated Maghnite is dried in an oven for 24 h at a temperature of 105 °C. Finally, Maghnite- $H^+$  was crushed, sieved and stored away from air and moisture.

### 2.3 Polymerization procedure

0.075 g of Maghnite- $H^+$  is heated before use under vacuum with mechanical stirring for 30 min. The polymerization was carried in bulk. The dried amount of Maghnite- $H^+$  is added to a flask containing 5 g of  $D_3^{\text{Ph,Me}}$ , the flask is immersed in an oil bath and brought to a temperature of 55 °C at while being stirred. After 150 min, the reaction was stopped by deactivating the Maghnite- $H^+$  by adding 1 ml of cold water to the reaction mixture. The Maghnite- $H^+$  is recovered by filtration, and the filtrate is precipitated in methanol (non-solvent). The insoluble product was dried at 80 °C in vacuum for 3-4 h and weighed as polymer. It was assumed that the residual material is the remaining monomers and the oligomers formed during the reaction. Regarding the kinetic study, the same procedure described above was repeated by changing the temperature, time and the percentage of the catalyst.

## 2.4 Characterization methods

### 2.4.1 X-ray Diffraction

The XRD patterns of the samples were carried out at room temperature on a Bruker D8 Advance X-Ray diffractometer (40 kV, 30 mA) with a graphite monochromator, using  $\text{CuK}\alpha$  radiation ( $\lambda = 0.154 \text{ nm}$ ) at the rate of  $5^\circ \text{ min}^{-1}$  in the range of  $2\theta = 2^\circ$  to  $80^\circ$ .

### 2.4.2 Infrared Spectroscopy

Infrared analysis of the polymers obtained was done using a Bruker Alpha FT-IR spectrometer equipped with an ATR accessory.

### 2.4.3 Nuclear Magnetic Resonance

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded under ambient temperature on Bruker Avance 300 NMR spectrometer, using tetramethylsilane as internal standard and deuterated chloroform as solvent.

### 2.4.4 Differential Scanning Calorimetry

The different thermal characteristics such as  $T_g$  of the synthesized polymer were measured by DSC from the corresponding thermal changes in the DSC thermogram using a Setaram 92 DSC apparatus. The specimen (approximately 10 mg) is heated at a rate of  $10^\circ \text{C/min}$  from  $-100$  to  $150^\circ \text{C}$  under a nitrogen atmosphere. The spectrum presented was obtained after a second heating.

### 2.4.5 Molecular Weight Measurements

Gel permeation chromatography (GPC) measurements of the samples was performed using a WISP Model 712, Waters Associates chromatograph, THF was used as a solvent and the apparatus was calibrated in an initial approximation with poly(methyl methacrylate) of known molecular weight.

### 3 Results and Discussion

#### 3.1 X-ray Diffraction (XRD)

Fig. 1 shows the characterization by XRD analysis of the raw Maghnite and Maghnite treated with sulfuric acid. It is obvious that the treatment led to the removal of minerals such as Calcite and Mica, this is confirmed by the decline of the intensity of their peaks compared to the strong peak corresponding to montmorillonite (green area), this elimination is clearer for the quartz, as shown by the reduction of the two peaks at  $2\theta = 21.93^\circ$  and  $26.71^\circ$  (blue areas). Moreover, the acid treatment caused a shift of the peak of montmorillonite to small values of  $2\theta$  from  $8.41^\circ$  to  $5.73^\circ$ , corresponding to an increase of the basal space of montmorillonite ( $d_{001}$ ) from  $10.50 \text{ \AA}$  to  $15.41 \text{ \AA}$ , this can be explained by the substitution of interlamellar cations of Maghnite by oxonium ions which have a larger atomic diameter.

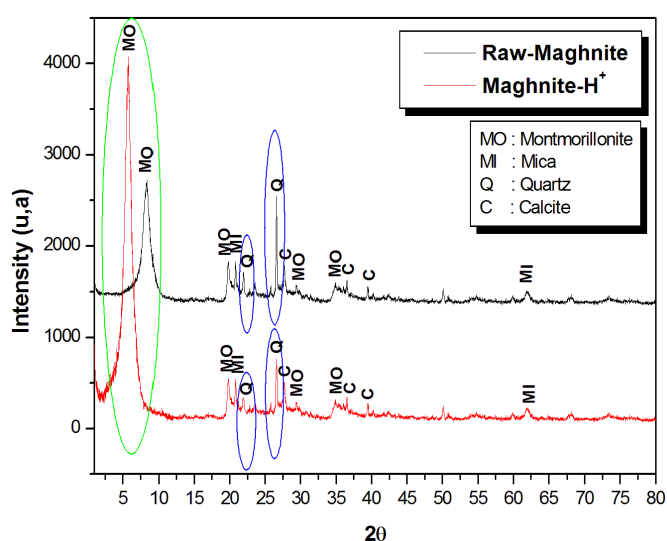


Fig. 1 XRD patterns of the Maghnite before treatment (Raw-Maghnite) and after treatment (Maghnite- $H^+$ )

#### 3.2 Infrared Spectroscopy (IR)

Fig. 2 provides the infrared spectra of the monomer and the obtained products for 90, 120, 150, 180 and 210 min at  $55^\circ\text{C}$ . The broad peak seen at  $3419 \text{ cm}^{-1}$  for the obtained products is attributed to the OH stretching of the Si-OH end groups in the PPMS chains, the appearance of this peak is due to the linkage between the released proton of Maghnite- $H^+$  and the oxygen atom at the end after the  $D_3^{\text{Ph,Me}}$  ring opening (Scheme 2a), the decrease in its intensity with time of the reaction is clearly noticeable, which may be explained by the increase of polymerization degree leading to smaller number of OH chain ends. The small peak appears at about  $3062 \text{ cm}^{-1}$  is attributed to the C-H bond of the phenyl ring. The two bands at  $2971$  and  $2925 \text{ cm}^{-1}$  are respectively due to C-H asymmetric/symmetric stretching of  $\text{CH}_3$ . The two bands seen respectively at  $2889$  and  $2843 \text{ cm}^{-1}$  are assigned to the C-H asymmetric/symmetric stretching of  $\text{CH}_2$ . The small series of bumps at  $1930$ ,  $1866$ ,  $1802$  and  $1757 \text{ cm}^{-1}$  are

caused by overtones (harmonics) of the phenyl ring vibrational modes having stretching frequencies in the fingerprint region. The bands occur in pairs, one at  $1601 \text{ cm}^{-1}$  and one at  $1483 \text{ cm}^{-1}$  are due to the C=C ring stretching absorptions. The signal at  $1272 \text{ cm}^{-1}$  is assigned to the  $\text{CH}_3$  symmetric deformation of Si- $\text{CH}_3$ . Peaks appearing at  $1026$ ,  $1108$  and  $478 \text{ cm}^{-1}$  are respectively attributed to the stretching vibrations and deformation vibrations of the linear Si-O-Si structures. The signal at  $816 \text{ cm}^{-1}$  is due to the Si-C stretching vibrations. The two bands at  $734$  and  $688 \text{ cm}^{-1}$  are assigned to the stretching vibrations of C-H in the phenyl ring. The infrared spectrum of obtained PPMS using Maghnite- $H^+$  as catalyst revealed no differences from those obtained by other researchers [30,31].

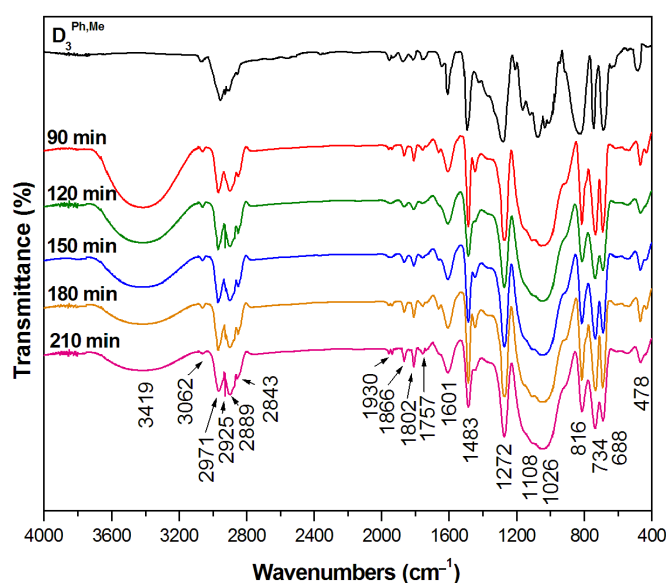
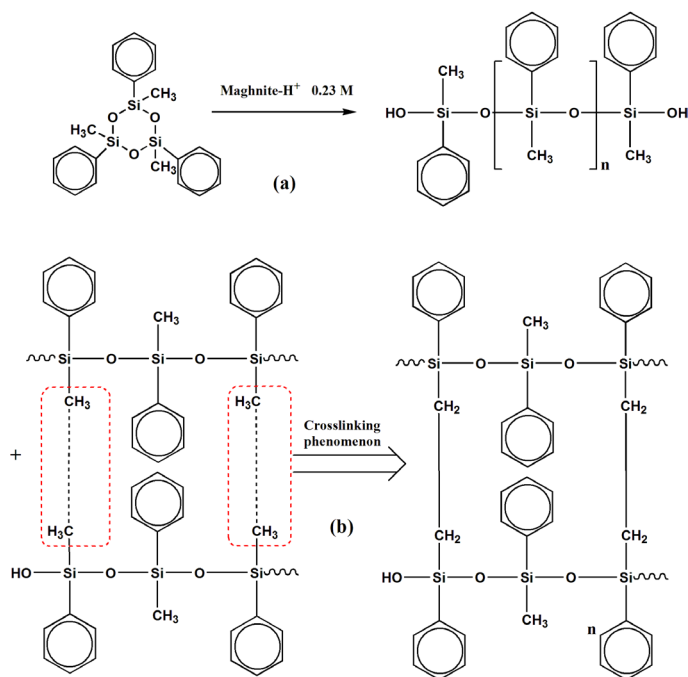


Fig. 2 IR spectra of PPMS obtained by the polymerization of  $D_3^{\text{Ph,Me}}$  at a temperature of  $55^\circ\text{C}$  for different times



Scheme 2 Polymerization of  $D_3^{\text{Ph,Me}}$  by Maghnite- $H^+$

### 3.3 Proton Nuclear Magnetic Resonance (<sup>1</sup>H NMR)

In order to identify more precisely the structure of the polymer obtained by the polymerization of D<sub>3</sub><sup>Ph,Me</sup> using the Maghnite-H<sup>+</sup> as catalyst, the product was analyzed before and after reaction by NMR analysis by comparing the two spectra: that of the monomer and that of polymer obtained at 55 °C for 150 min. The results are shown in Figs. 3a and 3b, which shows the different chemical shifts. In both spectra, the dominant peak observed at about 1.19 ppm, is attributed to the methyl groups. The neighboring peaks at 6.81, 6.94 and 7.18 ppm are assigned to the protons of the phenyl ring. The small peak appearing at 4.81 ppm is assigned to the OH groups at the ends of polymer chains during the reaction. Similar results were obtained by Fei et al. [32].

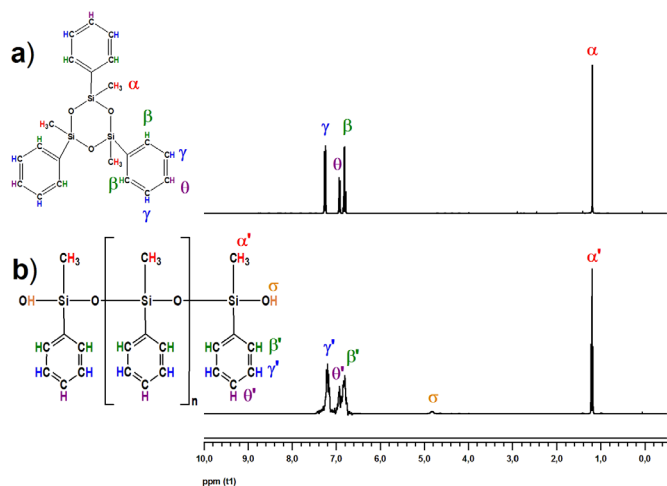


Fig. 3 <sup>1</sup>H NMR spectra of a) D<sub>3</sub><sup>Ph,Me</sup> and b) polymer obtained at a temperature of 55 °C for 150 min

### 3.4 Carbon Nuclear Magnetic Resonance (<sup>13</sup>C NMR)

It was therefore necessary to analyze the products obtained by <sup>13</sup>C NMR to provide a complement to the previous study. The results are shown in Fig. 4 (a, b and c) showing the <sup>13</sup>C NMR spectra of the monomer, the polymer obtained after 150 min and after 180 min respectively. The peak located at approximately -0.12 ppm for the monomer and 0.39 ppm for the polymers corresponds to the carbon of CH<sub>3</sub>. The peaks at 137.85, 130.39, 128.76 and 126.66 ppm for the monomer, and at 137.96, 131.44, 128.77 and 125.08 ppm for the two polymers are assigned to the phenyl ring carbons as shown in Fig. 4.

Moreover, there is a creation of a down peak at 32.87 ppm on the DEPT-135 spectrum of the polymer obtained after 180 min, that is attributed to the carbon of CH<sub>2</sub>, indicating the formation of ethylene bridges between linear polymer chains (Scheme 2b). These results show that beyond 180 min of reaction time, the polymer chains can be crosslinked to form organopolysiloxane elastomers.

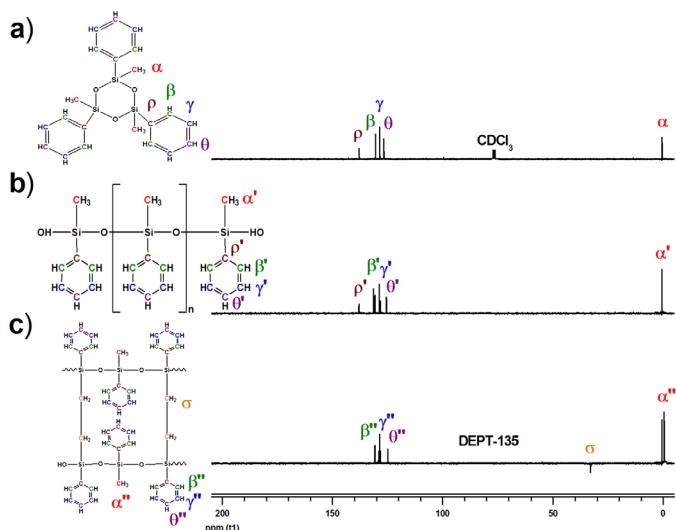


Fig. 4 <sup>13</sup>C NMR spectra of a) D<sub>3</sub><sup>Ph,Me</sup>, b) polymer obtained after 150 min and c) polymer obtained after 180 min at a temperature of 55 °C

### 3.5 Differential Scanning Calorimetry (DSC)

DSC was used as a thermal analysis, to identify and confirm at the same time the structure and the purity of the obtained product. Fig. 5 shows the DSC thermogram of the polymer obtained after 150 min of reaction time. The thermogram shows a small thermal deformation at about -37.02 °C, which corresponds to the glass temperature of the polymer (T<sub>g</sub> = -37.02 °C), this T<sub>g</sub> value is comparable to that of linear PPMS. The result obtained by DSC largely supports the results obtained by IR and NMR for the linear structure of the polymer obtained after 150 min, it also simulates to a large extent the results obtained in previous research [33,34].

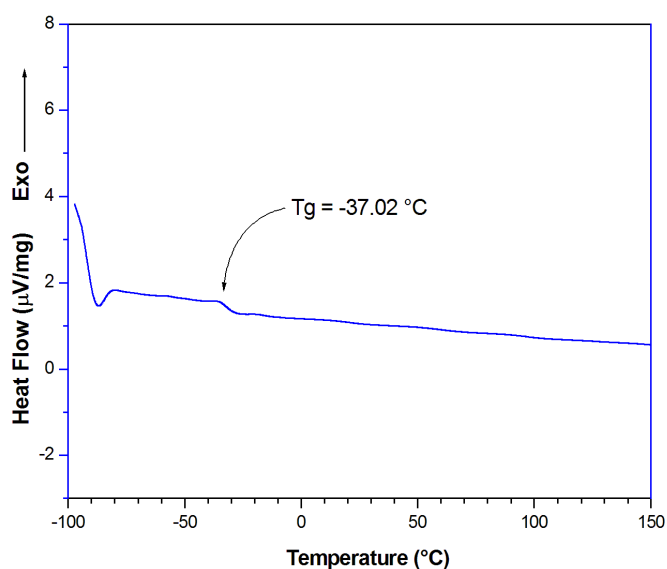


Fig. 5 DSC thermogram of obtained PPMS obtained after 150 min

### 3.6 Effect of temperature

In an effort to understand and control more the polymerization reaction of  $D_3^{\text{Ph,Me}}$  catalyzed by Maghnite- $H^+$ , we have examined the effect of the temperature of the medium on the reaction that takes place there. Table 1 gives measured values of the monomer conversion and number average molecular mass of the polymers obtained in a temperature range of 40 to 70 °C. Fig. 6 shows the gel permeation chromatograms of the polymers obtained at different temperatures. The increase in temperature leads to a significant increase in conversion reaching 88% at 55 °C, beyond this temperature, this increase becomes negligible until the conversion stabilizes at its maximum at about 91%. On the other hand, the variation in average molecular mass shows two different behaviors, a gradual increase from 40 to 55 °C, followed by a reduction after just exceed its highest value at about 55 °C, we assume that it is the ceiling temperature, this decrease in average molecular mass can be explained by the fragmentation of the chains suggests the thermal decomposition of PPMS after the breaking of Si-O bonds when approaching the boiling point. The thermal degradation phenomenon reflects a wide divergence between the molecular mass values, resulting in the increase of the polydispersity index, which is found in Table 1.

**Table 1** Effect of reaction temperature on  $D_3^{\text{Ph,Me}}$  polymerization<sup>a</sup>

T(°C)	Conversion of Monomer (wt %)	$M_n$ (g/mol)	$M_w / M_n$
40	41	2650	1.06
45	69	9425	1.08
50	72	16248	1.12
55	88	27514	1.13
60	90	24347	1.55
65	91	19998	1.74
70	91	12478	1.91

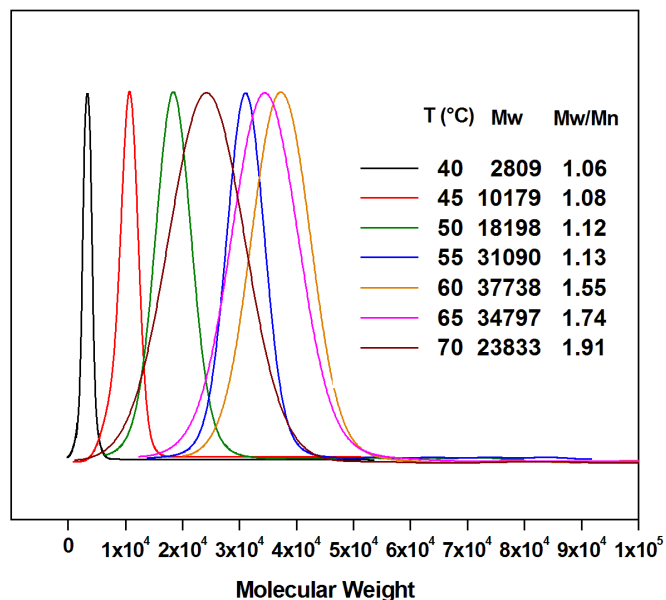
<sup>a</sup> Maghnite- $H^+$  /  $D_3^{\text{Ph,Me}}$  weight ratio = 1.5%. Reaction time 150 min.

$M_n$  : Number average molecular mass;

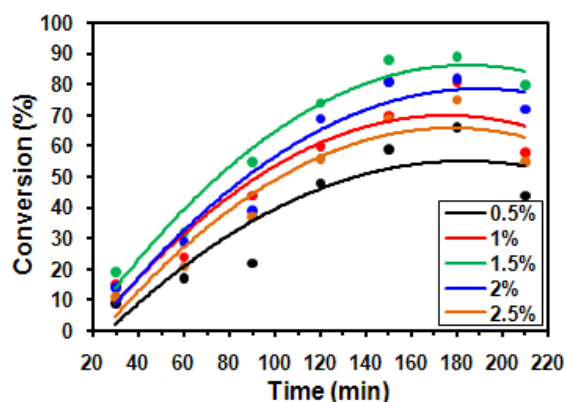
$M_w / M_n$  : Polydispersity index.

### 3.7 Effect of Maghnite- $H^+$ /Monomer weight ratio

In order to study the catalytic action of Maghnite- $H^+$  as a heterogeneous catalyst in the polymerization reaction of  $D_3^{\text{Ph,Me}}$ , we performed the reaction with a catalyst content ranging from 0.5 to 2.5% by weight, so that for each catalyst content, the reaction time varied from 30 to 210 min. The results of the influence of the Maghnite- $H^+$  content on the monomer conversion and on the number average molecular mass are shown in Fig. 7 and 8 respectively. In all tests, the reaction was carried out in bulk and at a temperature of 55 °C. It is clearly noticeable that for all the different Maghnite- $H^+$  contents, the reaction time has an effect proportionally positive on the monomer conversion before 180 min. After this duration, the effect of reaction time has become negative (Fig. 7).



**Fig. 6** Gel permeation chromatograms of the polymers obtained at different temperatures



**Fig. 7** Effect of Maghnite- $H^+$ / $D_3^{\text{Ph,Me}}$  weight ratio on the conversion of monomer

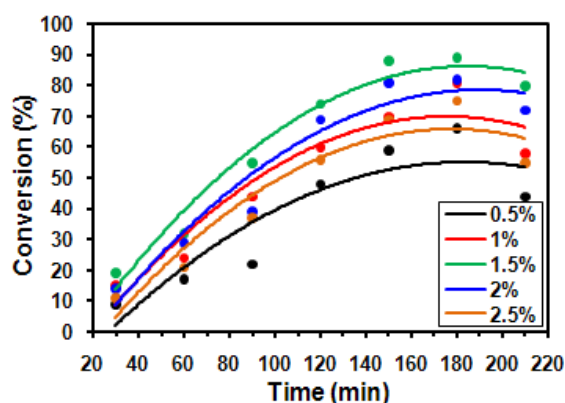
The reduction in the monomer conversion for large periods may be explained by the occurrence of depolymerization phenomenon of polymer chains caused by the active sites of the Maghnite- $H^+$  still remaining in the reaction medium. This result indicates that the Maghnite- $H^+$  can play the opposite role after periods of time sufficiently large. Similar results were obtained in previous studies [7,8]. On the other hand, the average molecular mass increases with increasing reaction time, the maximum value for the different Maghnite- $H^+$  contents is about 150 min, then it stabilizes almost up to 180 min, so that it begins to decrease. The reduction over time, of the peak corresponding to OH groups which exist only at the end of the polymer chains of PPMS synthesized by Maghnite- $H^+$  showing by the infrared analysis (Fig. 2), indicates that the chains became longer, resulting in large molecular mass. The temporary stabilization between 150 and 180 min of the average molecular mass is due to the crosslinking phenomenon, leading to branched structures because of the formation of ethylene bridges between the linear chains, this explanation is clearly supported by what has been

obtained by  $^{13}\text{C}$  NMR analysis (Fig. 4c). The decrease in the average molecular mass after 180 min can be explained by backbiting degradation in the growing polymer chains, which generates oligomers and cyclic polysiloxanes of varying sizes, thereby increasing the polydispersity index (Table 2).

**Table 2** Kinetic evolution of  $\text{D}_3^{\text{Ph,Me}}$  polymerization<sup>a</sup> initiated by Maghnite- $\text{H}^+$

Time (min)	Conversion of Monomer (wt %)	$M_n$ (g/mol)	$M_w/M_n$
30	19	8557	1.02
60	32	11470	1.04
90	55	17488	1.05
120	74	23478	1.08
150	88	27514	1.13
180	89	26666	1.17
210	80	18524	1.31

<sup>a</sup> Maghnite- $\text{H}^+$ /  $\text{D}_3^{\text{Ph,Me}}$  weight ratio = 1.5%. Reaction temperature 55°C.



**Fig. 8** Effect of Maghnite- $\text{H}^+$ / $\text{D}_3^{\text{Ph,Me}}$  weight ratio on the average molecular mass

### 3.8 Kinetics of the polymerization reaction

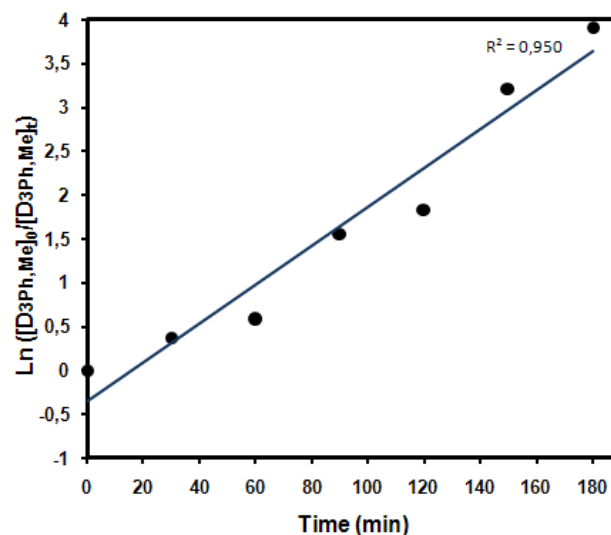
In order to study the chemical kinetics of the polymerization reaction of  $\text{D}_3^{\text{Ph,Me}}$  catalyzed by Maghnite- $\text{H}^+$ , we followed the evolution of the concentration of monomer over time, we were interested just for  $t \leq 180$  min, where there was not the depolymerization phenomenon. The results clearly indicate that the reaction is first-order with respect to monomer (Fig. 9).

### 4 Conclusion

Maghnite- $\text{H}^+$  showed an excellent catalytic capacity for the synthesis of polyphenylmethylsiloxane. The reaction was carried out under mild conditions and without the use of the solvent, Maghnite- $\text{H}^+$  was removed at the end of the reaction by simple filtration, which is largely in accordance with the principles of green chemistry. IR analysis confirmed the chemical structure of different polymers obtained, the presence of the OH group on the IR spectra indicates that they are linear polymers. NMR analysis showed that after a period of 150 min,

the polymer began to crosslink by establishing interchain bonds between the methyl groups attached to the silicon atom.

The study of the variation of the average molecular mass as a function of temperature informs us that the ceiling temperature of this polymerization is 55 °C, beyond which the polymer can be depolymerized. The kinetic study demonstrated that the reaction is of the first order with respect to the monomer.



**Fig. 9** First order kinetics for the polymerization of  $\text{D}_3^{\text{Ph,Me}}$  by Maghnite- $\text{H}^+$  (In bulk,  $T = 65^\circ\text{C}$  and Mass content of catalyst = 1.5%)

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