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Acid-activated bentonite (Maghnite-H+) as a novel catalyst for the polymerization of decamethylcyclopentasiloxane

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Abstract. In this study, we propose Maghnite-H+, as an ecological, cost-effective and easily renewable catalyst, for the polymerization of decamethylcyclopentasiloxane (D5). The Maghnite is a clay consisting primarily of smectite minerals (montmorillonite group), which can be activated/reactivated through a simple process, by replacing interlayer cations by protons. Linear polymers with higher molecular mass and narrower molecular mass distribution (MMD) can be obtained with less cyclic by-products, using Maghnite-H+. The reaction was investigated in bulk, taking into account the effect of time, temperature and amount of catalyst on the monomer conversion and MMD. When the yield rises to 96%, the MMD is broadened, suggesting the formation of cyclic oligomers and/or crosslinking bonds, this was confirmed experimentally by infra-red spectroscopy, proton nuclear magnetic resonance (^{1}H NMR) and ^{13}C NMR analyses. The kinetics have been also studied; the reaction is first order in the monomer. The proposed reaction mechanism shows clearly the role of Maghnite-H+ for D5 polymerization.
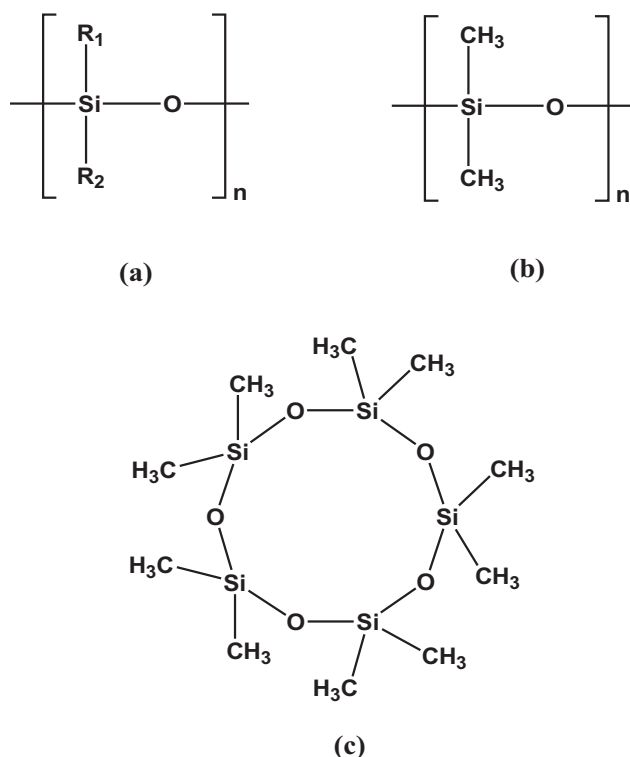
Keywords. Catalyst; maghnite-H+; bentonite; decamethylcyclopentasiloxane; ring opening polymerization.

1. Introduction

The substitution of traditional homogeneous catalysts of Lewis and Brönsted acids, which are heterogeneous, has now become the main concern for researchers in the field of polymers, because solid acid catalysts can constitute a greener and more sustainable alternative for the polymerization process. Such catalysts offer a number of advantages compared with their homogeneous counterparts: milder reaction conditions, no need for solvents or the use of less toxic materials and easy separation from the reaction mixture by simple filtration, etc. [1,2].

Much work has been carried out on the polymerization of siloxane monomers and their derivatives. Starting with the research carried out by Friedel and Crafts, which synthesized the first polysiloxane in 1877 [3,4]. Today, silicones are seeing a great development thanks to their outstanding physicochemical properties, which are essentially due to the inorganic backbone formed by linking Si–O–Si (scheme 1a). This provides a very good thermal stability and excellent chemical inertness because of the remarkable strength of the Si–O bond. This bond is in particular very resistant to oxidation and hydrolysis [5–7].

Polydimethylsiloxane (PDMS) represents the most important family of organosilicon polymers from industrial applications point of view (scheme 1b). The most common pathways used for the synthesis of these products are the anionic and cationic ring opening polymerization, leading mainly to linear polymers [8,9]; without neglecting certain amount of cyclic structures arising from side reactions such as the backbiting and redistribution reactions, which causes the broadening of the molecular mass distribution (MMD) [10,11], the yield of cyclic structures depends primarily on the type of catalyst used and process conditions. The polymerization of the siloxane monomers was performed by different procedures using a variety of catalysts, like phosphazene bases [12,13], strong bases [14,15], dodecylbenzenesulphonic acid [16], triflic acid [17], tris(pentafluorophenyl)borane [18], trifluoromethanesulphonic acid [19], etc. The solid catalysts most used for the polymerization of siloxanes are metals, in particular copper. The methylchlorosilanes used for the synthesis of methyl silicones, such as PDMS, are prepared by reacting silicon with methyl chloride at 300°C, in the presence of copper (about 10% by weight with respect to silicon). Other metals are also sometimes added (aluminium, zinc) to further increase the yield of the

(a)

(b)

(c)

Scheme 1. The structure of **(a)** polysiloxane, **(b)** polydimethylsiloxane and **(c)** decamethylcyclopentasiloxane.

reaction. The various chlorosilanes obtained (dimethyldichlorosilanes, methyltrichlorosilanes, methyldichlorosilanes, trimethylchlorosilanes, etc.) are then separated by distillation [20].

The purpose of this work is to obtain polymers of PDMS type by replacing the conventional homogeneous catalysts with a new non-toxic heterogeneous catalyst prepared by simple activation of natural clay. The originality of the method lies in the use of Maghnite-H$^+$ (Algerian clay) for the polymerization of D5 (scheme 1c). Maghnite is characterized by a high ratio of SiO_2 to Al_2O_3 compared with other clays; it becomes higher in Maghnite-H$^+$ [21,22]; this property gives it a great ability to capture protons, because the SiO_2 molecule is less electronegative than that of Al_2O_3, which leads to a good activation. This source was used for the preparation of clay-based nanocomposites [23–25], also for the polymerization of different monomers, like N-vinyl-2-pyrrolidone [26] and ε-caprolactone [27], but not yet for the polymerization of siloxane monomers. Techniques such as infra-red (IR) spectroscopy, proton nuclear magnetic resonance (^{1}H NMR) and ^{13}C NMR were used to characterize the obtained D5. Moreover, the interchain linkages due to the crosslinking phenomenon and the undesirable cyclic structures formed in long periods of time have been clearly shown. The thermal stability of obtained polymers was studied by differential scanning calorimetry (DSC) analysis. The variation in monomer conversion and MMD according to temperature, time and weight

percentage of Maghnite-H$^+$ has been well discussed. At the end, we propose a reaction mechanism, in which we show the role of the Maghnite-H$^+$ during the various stages of polymerization.

2. Experimental

2.1 *Materials*

Decamethylcyclopentasiloxane (D5, 98%) and all other products were used as purchased from the Aldrich Chemical Annex in Algeria, without further purification. Methanol was purified by vacuum distillation. Maghnite was obtained from an Algerian company of bentonite (BENTAL), without any pretreatment.

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

In a beaker, a mass of 30 g of raw Maghnite was combined with 120 ml of distilled water at the temperature of 25°C and the suspension is left under stirring. After 30 min, 100 ml of a solution of sulphuric acid (0.23 M) was added, and the stirring was continued for 48 h. After filtration and subsequent washing, the activated Maghnite was dried in an oven for 24 h at the temperature of 105°C. Finally, the resulting Maghnite-H$^+$ was crushed, sieved and stored away from air and moisture.

2.3 *Polymerization procedure*

Maghnite-H$^+$ powder (0.15 g) was heated at 120°C before use in vacuum (1 bar) with mechanical stirring for 30 min. The polymerization was carried out without using solvent. The dried amount of prepared Maghnite-H$^+$ was added to a flask containing 5 g of D5 and the flask was immersed in an oil bath and brought to the temperature of 50°C while being stirred. After 8 h, the reaction was stopped by deactivating the Maghnite-H$^+$ by adding cold water to the reaction mixture. The Maghnite-H$^+$ was recovered by filtration, and the filtrate was precipitated in methanol (non-solvent). The insoluble product was filtered, dried at 80°C in vacuum (1 bar) for 6–8 h and weighed as a polymer. Excess water was retrieved by evaporation at 105°C. It was assumed that the residual material was the remaining monomers and the oligomers formed during the reaction. Regarding the kinetic study, the same procedure described earlier was repeated by changing the temperature, time and the percentage of Maghnite-H$^+$.

2.4 *Characterization methods*

2.4a *X-ray diffraction*:   The X-ray diffraction (XRD) patterns of the samples were obtained at room temperature on a Bruker D8 Advance X-Ray diffractometer (40 kV, 30 mA) with a graphite monochromator, using CuKα radiation (λ = 0.154 nm) at the rate of 5° min^{-1} in the range of $2\theta = 2$–80°.

2.4b   *IR spectroscopy*:   IR analysis of the polymers obtained was performed using a Bruker Alpha FT-IR spectrometer equipped with an ATR accessory.

2.4c   *NMR*: ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature on a Bruker Avance 300 NMR spectrometer, using tetramethylsilane as the internal standard and deuterated chloroform as solvent.

2.4d   *DSC*:   Various thermal characteristics, such as T_g, T_c and T_m of the synthesized polymer, were measured by DSC from the corresponding thermal changes in the DSC thermogram using a Setaram 92 DSC apparatus.

2.4e   *Molecular weight measurements*:   Gel permeation chromatography (GPC) measurements of the samples were 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 polymethyl methacrylate of known molecular weight.

3.   Results and discussion

3.1   *XRD*

Figure 1 shows the characterization by XRD analysis of the raw Maghnite and Maghnite treated with sulphuric 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 with the strong
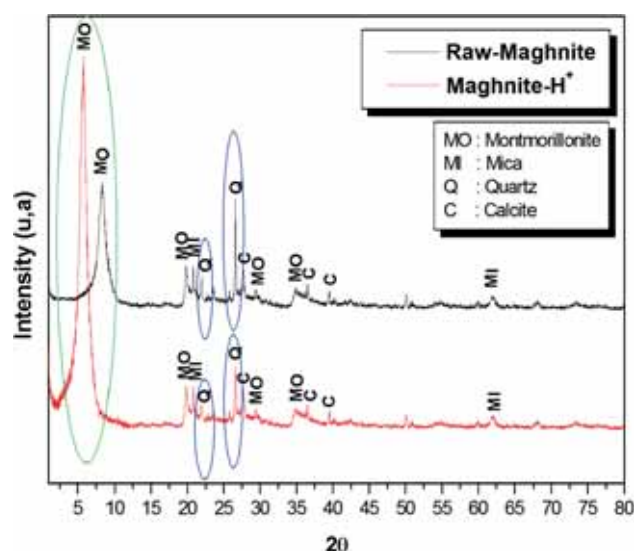

Figure 1.   XRD patterns of the Maghnite before treatment (Raw-Maghnite) and after treatment (Maghnite-H$^+$).
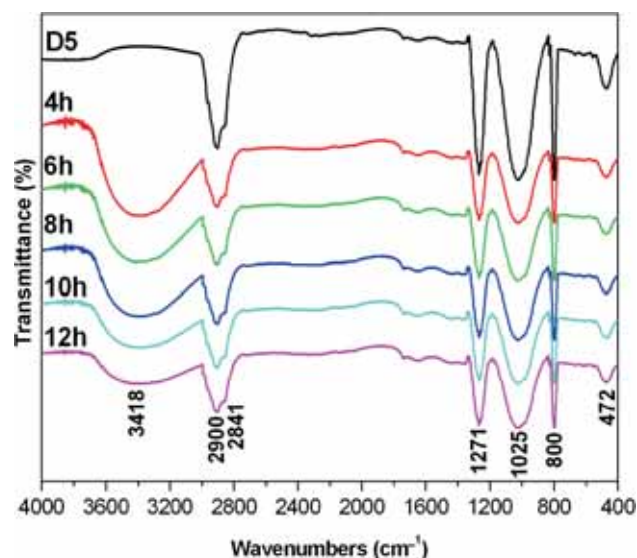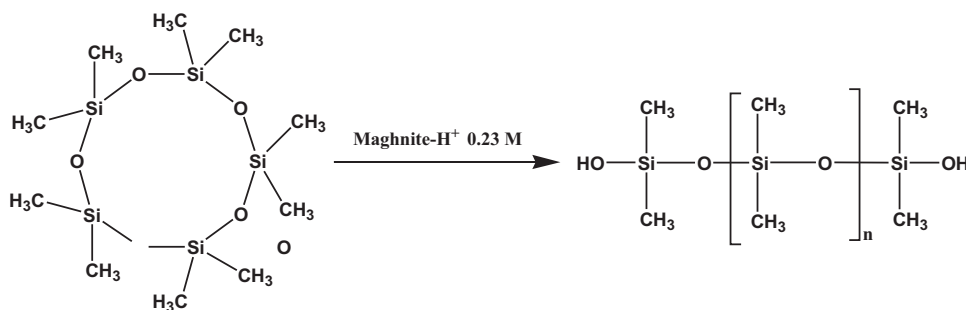

Figure 2.   IR spectra of PDMS obtained by the polymerization of D5 at the temperature of 50°C for different times.

peak corresponding to montmorillonite (green area); this elimination is clearer for the quartz, as shown by the reduction of the two peaks at $2\theta = 21.93$ and $26.71°$ (blue areas). Moreover, the acid treatment caused a shift of the peak of montmorillonite to smaller values of 2θ from 8.41 to 5.73°, corresponding to an increase of the interlayer distance of montmorillonite (d_{001}) from 10.50 to 15.41 Å; this can be explained by the substitution of interlamellar cations of Maghnite by the hydronium ions (H_3O^+); which have a larger atomic diameter.

3.2   *IR spectroscopy*

Figure 2 shows the IR spectra of the monomer and the obtained products for 4, 6, 8, 10 and 12 h at 50°C. The broad peak seen at 3418 cm^{-1} for the obtained products is attributed to the OH stretching of the Si–OH end groups in the PDMS 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 D5 ring opening (scheme 2); 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 two bands at 2900 and 2841 cm^{-1} are, respectively, due to C–H asymmetric and symmetric stretching of CH$_3$. The signal at 1271 cm^{-1} is assigned to the CH$_3$ symmetric deformation of Si–CH$_3$. Peaks appearing at 1025 and 472 cm^{-1} are, respectively, attributed to the stretching vibrations and deformation vibrations of the linear Si–O–Si structures. The signal at 800 cm^{-1} is due to the Si–C stretching vibrations. The IR spectrum of obtained PDMS using Maghnite-H$^+$ as catalyst revealed no differences from those obtained by other researchers [28,29].

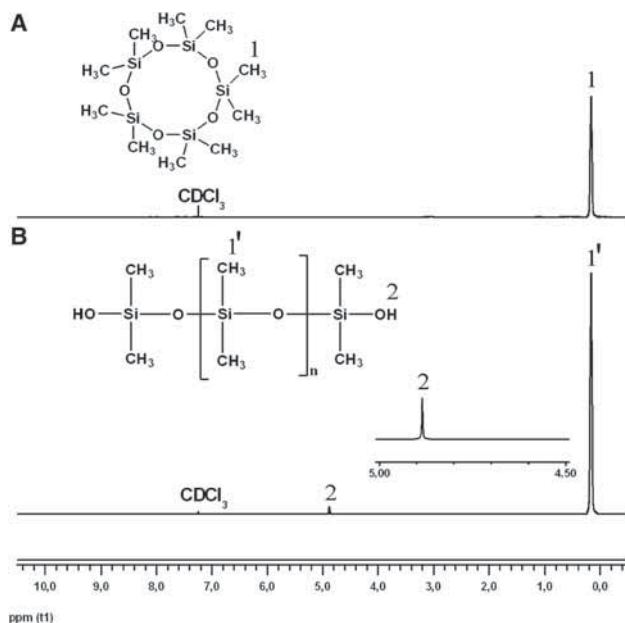**Scheme 2.** Polymerization of D5 by Maghnite-H$^+$.

Figure 3. ^{1}H NMR spectra of **(A)** D5 and **(B)** polymer obtained at the temperature of 50°C for 8 h.

Figure 4. ^{13}C NMR spectra of **(A)** D5, **(B)** polymer obtained after 8 h and **(C)** polymer obtained after 10 h at the temperature of 50°C.

3.3 ^{1}H NMR

In order to identify more precisely the structure of the polymer obtained by the polymerization of D5 using the Maghnite-H$^+$ as catalyst, the product was analysed before and after reaction by NMR analysis by comparing the two spectra: that of the monomer and that of polymer obtained at 50°C for 8 h. The results are shown in figure 3, which shows the different chemical shifts. In both spectra, the dominant peak observed at about 0.14 ppm is attributed to the methyl groups; it is more intense in the spectrum of the polymer, implying a large number of methyl groups in the polymeric chain. The small peak appearing at 4.88 ppm is assigned to the OH groups at the ends of polymer chains during the reaction. Similar results were obtained by Ramli *et al* [30].
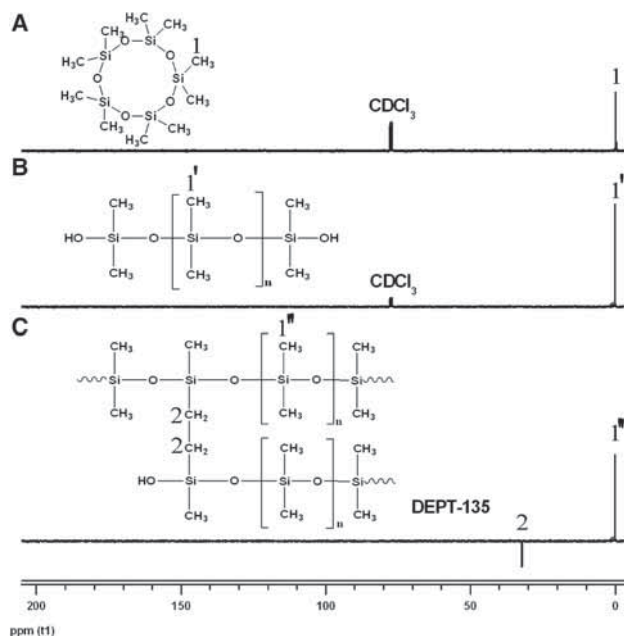
3.4 ^{13}C NMR

It was necessary to analyse the products obtained by ^{13}C NMR to provide a complement to the previous study. The results are shown in figure 4. The spectrum of the monomer is characterized by a single peak at approximately –0.43 ppm, corresponding to the carbon of CH$_3$ (curve above). The other two spectra correspond to ^{13}C NMR spectrum of the polymer obtained after 8 h (curve in the middle) and the DEPT-135 spectrum of the polymer obtained after 10 h (curve below). Both spectra have a characteristic peak at 0.1 ppm, which corresponds to methyl groups in the polymer chain. Moreover, there is a creation of a down peak at 32.1 ppm for the polymer obtained after 10 h, which is attributed to the carbon of CH$_2$, indicating the formation of ethylene bridges between linear polymer chains. These results show that beyond 8 h of
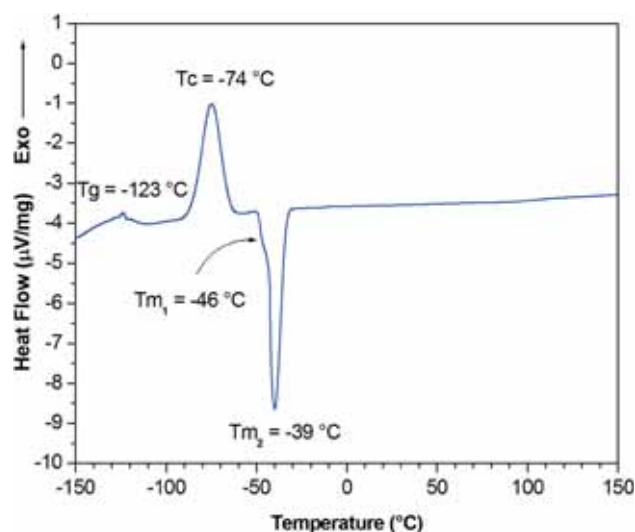
Figure 5. DSC thermogram of the obtained PDMS.

reaction time, the polymer chains can be crosslinked to form organopolysiloxane elastomers.

3.5 *DSC*

DSC was used as a thermal analysis, to identify and test at the same time the purity of the product obtained. Figure 5 shows the DSC thermogram of the polymer obtained after 8 h of reaction time. The thermogram presents a glass transition, exothermic peak and two endothermic peaks. The T_g is located at –123°C. The exothermic peak (T_c) detected at –74°C corresponds to the cold crystallization phenomenon, indicating the existence of amorphous regions. The multiple endothermic peaks appear around –46 and –39°C corresponding to the melting temperature, related to the fact that there are different crystalline forms in the polymer. These results are consistent to a large extent with those found in previous studies [31,32].

3.6 *Effect of temperature*

In an effort to understand and control the polymerization reaction of D5 catalysed by Maghnite-H$^+$ more, 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 the temperature range of 20–100°C. The increase in temperature leads to a significant increase in conversion, reaching 94% at 50°C; beyond this temperature, this increase becomes negligible until the conversion stabilizes at its maximum at about 80°C. On the other hand, the variation in average molecular mass shows two different behaviours: a gradual increase from 20 to 50°C, followed by a reduction after just exceeding its highest value at about 50°C; we assume that this is the ceiling temperature; this

Table 1. Effect of reaction temperature on D5 polymerization.[a]

T (°C)	Conversion of monomer (wt%)	M_n	M_w/M_n
20	23	16217	1.09
30	49	35200	1.13
40	67	69780	1.13
50	94	105214	1.15
60	95	99995	1.28
80	96	62047	1.30
100	96	41513	1.45

[a]Maghnite-H$^+$ − D5 weight ratio = 3%. Reaction time = 8 h.
M_n: number-average-molecular mass;
M_w/M_n: polydispersity index.

decrease in average molecular mass, which can be explained by the fragmentation of the chains, suggests thermal decomposition of PDMS 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 presented in table 1.

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 D5, we performed the reaction with a catalyst content ranging from 1 to 5% by weight, so that for each catalyst content, the reaction time varied from 1 to 12 h. The results of the influence of the Maghnite-H$^+$ content on the monomer conversion and on the number average molecular mass are shown in figures 6 and 7, respectively. In all tests, the reaction was carried out in bulk and at the temperature of 50°C. It is clearly noticeable that for all the different Maghnite-H$^+$ contents, the reaction time has an effect that is proportionally positive on the monomer conversion before 10 h. After this duration, the effect of reaction time has become negative (figure 6). 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 previously obtained by several authors [33,34]. Moreover, the conversion of the monomer decreased when we used more than 3% of Maghnite-H$^+$. This is due to the existence of a large number of active sites carried on the surface of montmorillonite, which in turn begins to attack the polymer chains in place of the monomer rings, resulting in the breaking of these chains and the formation of the oligomers. On the other hand, the average molecular mass increases with increasing reaction time; the maximum value for the different Maghnite-H$^+$ contents is about 8 h; later it almost stabilizes for 2 h, so that it begins to decrease. The reduction over
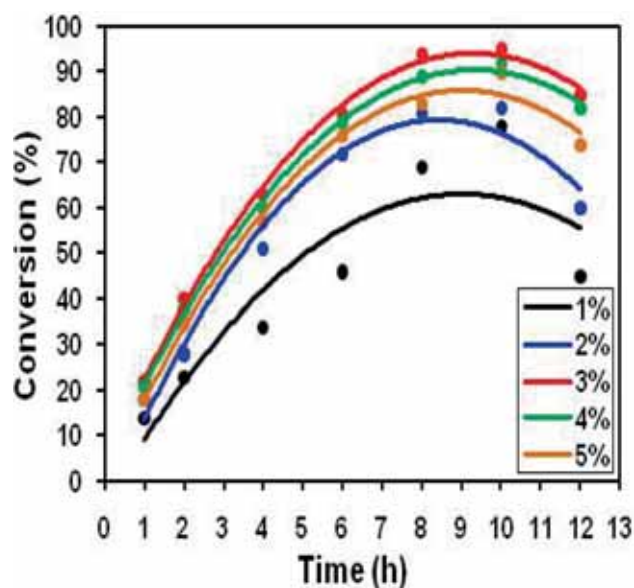
Figure 6. Effect of Maghnite-H$^+$–D5 weight ratio on the conversion of monomer.
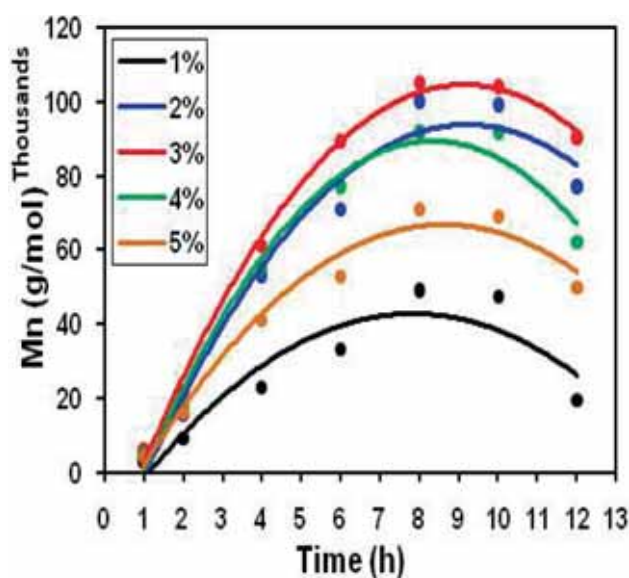

Figure 7. Effect of Maghnite-H$^+$–D5 weight ratio on the average molecular mass.

time of the peak corresponding to OH groups occurs only for the end of the polymer chains of PDMS synthesized by Maghnite-H$^+$ as shown by the IR analysis (figure 2), indicating that the chains become longer, resulting in large molecular mass. The temporary stabilization between 8 and 10 h of the average molecular mass and at the same time the increase in the monomer conversion, due to the crosslinking phenomenon, leads 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}C NMR analysis (figure 4). The decrease in the average molecular

Table 2. Kinetic evolution of D5 polymerization[a] initiated by Maghnite-H$^+$.

Time (h)	Conversion of monomer (wt%)	M_n	M_w/M_n
1	22	6213	1.11
2	40	22147	1.10
4	69	61254	1.12
6	84	89526	1.13
8	94	105214	1.15
10	96	104147	1.41
12	85	90514	1.35

[a]Maghnite-H$^+$ − D5 weight ratio = 3%. Reaction temperature = 50°C.

Table 3. The conversion obtained for the synthesis of polysiloxane with different catalysts.

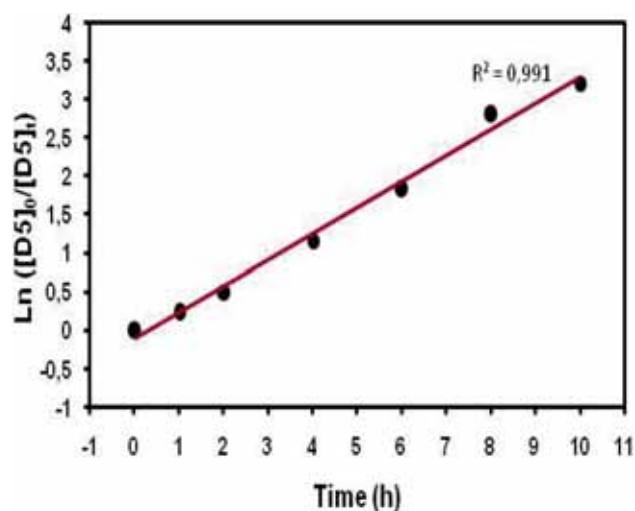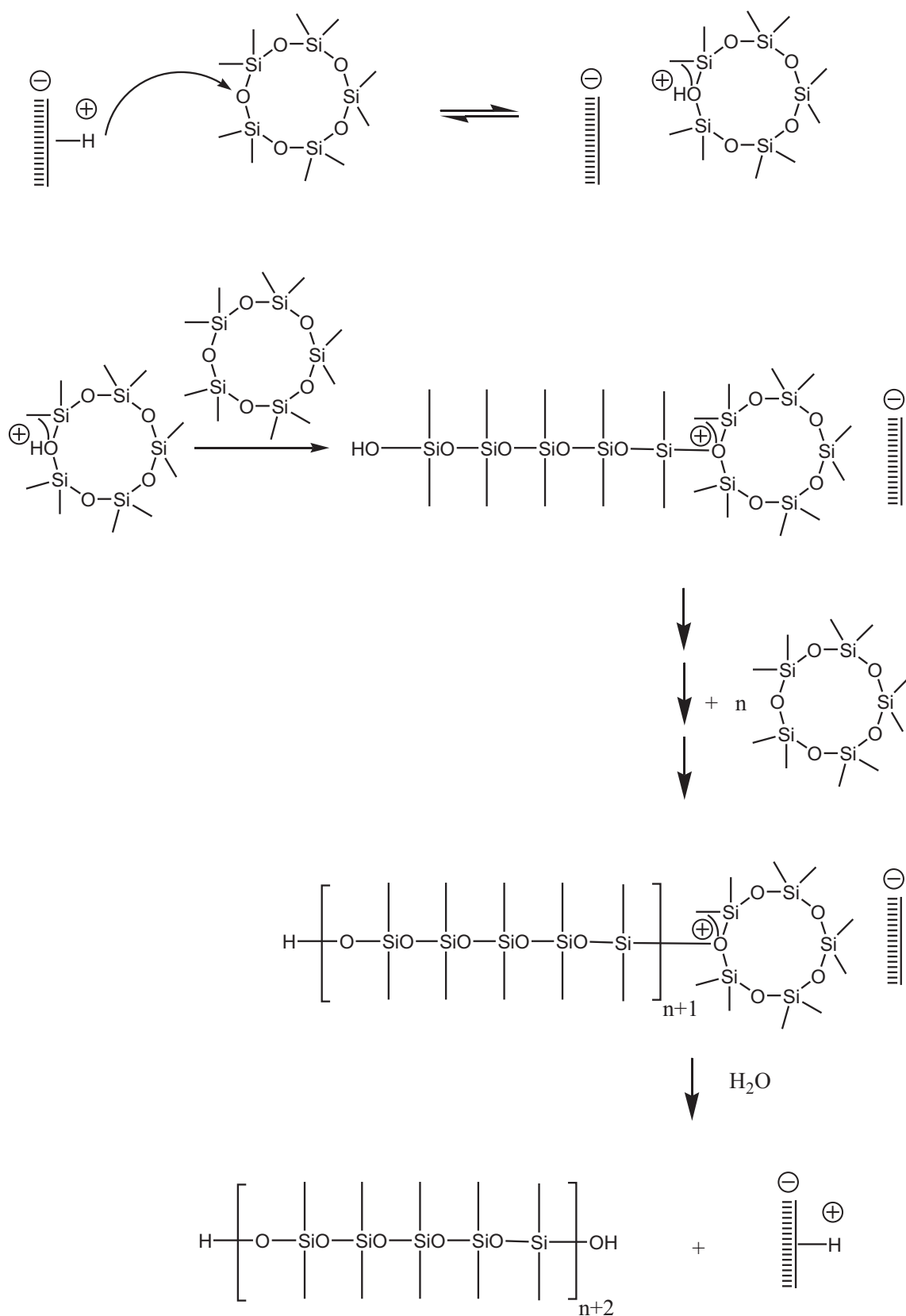| Catalyst	Conversion of monomer (wt%)	References
Phosphazene bases	95	[12,13]
Strong bases	90	[14,15]
Triflic acid	77	[17]
Dodecylbenzenesulphonic acid	85	[29]
Trifluoromethanesulphonic acid	58	[19]
Tris(pentafluorophenyl)borane	95	[18]
Maghnite-H$^+$	94	
Maghnite-H$^+$ used	94	

Figure 8. Representation of ln([D5]$_0$/[D5]$_t$) as a function of time (Maghnite-H$^+$–D5 weight ratio = 3%, T = 50°C).

mass after 10 h 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). In general, Maghnite-H$^+$

Scheme 3. Mechanism of D5 polymerization catalysed by Maghnite-H$^+$.

shows excellent catalytic capacity, leading to a conversion that is in some cases superior to those obtained by other catalysts in the form of acidic and basic species. The reuse of Maghnite-H$^+$ gave the same conversion of the monomer as that in its first use. Table 3 summarizes the conversion obtained using Maghnite-H$^+$, Maghnite-H$^+$ used and other catalysts previously used by several authors for the polymerization of siloxane monomers.

3.8 *Kinetics and mechanism of the polymerization*

In order to study the chemical kinetics of the polymerization reaction of D5 catalysed by Maghnite-H$^+$, we followed the evolution of the concentration of monomer over time; we were interested just for $t \leq 10$ h, where there was no depolymerization phenomenon. The results clearly indicate that the reaction was first-order with respect to the monomer (figure 8). Scheme 3 shows the probable reaction mechanism.

4. Conclusions

The cationic ring opening polymerization of decamethylcyclopentasiloxane was carried out by heterogeneous catalysis in bulk, using the Maghnite-H$^+$ as green and ecological catalyst. The reaction conversion achieved with a Maghnite-H$^+$ content of 3% by weight was about 94%, at 50°C for 8 h. The product obtained was a linear polymer: the polysiloxane. The polymer was characterized by different methods of analysis, such as IR, ^{1}H NMR, ^{13}C NMR, DSC and GPC.

Among the results obtained, the Maghnite-H$^+$ has served as a catalyst support with an optimum content of 3% by weight; above this threshold, it becomes a depolymerizing agent, also causing a broadening of the MMD. The Maghnite-H$^+$ is less expensive and less dangerous than the catalysts used in the synthesis of polysiloxanes reported in previous work.

^{13}C NMR analysis confirmed the cyclic structure of polymer obtained after 10 h. The molecular masses are significant and increase with the reaction time ($t \leq 8$ h). The DSC analysis showed a glass transition temperature and a melting temperature similar to those obtained in earlier studies using other catalysts.

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