



Research Article

Green Polymerization of Hexadecamethylcyclooctasiloxane Using an Algerian Proton Exchanged Clay Called Maghnite-H⁺

Djamal Eddine Kherroub^{1,2*}, Mohammed Belbachir¹, Saad Lamouri³

¹Laboratory of Polymer Chemistry, Department of Chemistry, Faculty of Exact and Applied Sciences, University of Oran 1 Ahmed Ben Bella, BP 1524 El'Menouer Oran 31000, Algeria

²University Centre of Relizane Ahmed Zabana, Institute of Sciences and Technology, BP 48000, Algeria

³Laboratory of Macromolecular Chemistry, Polytechnic Military School (EMP), Bordj El Bahri, 16111 Algiers, Algeria

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Abstract

The purpose of this study was to synthesize polydimethylsiloxanes by heterogeneous catalysis, based on the polymerization of the hexadecamethylcyclooctasiloxane (D8) by an environment-friendly solid catalyst (Maghnite-H⁺). Maghnite-H⁺ is a natural Algerian clay of the montmorillonite type, prepared by activation with sulfuric acid, the impact of this activation was observable in the XRD spectrum, by the increase in the interlayer spacing (d_{001}) resulting from the intercalation of hydronium ions between layers. The molecular structure of the obtained polymer was determined by different chemical methods of analysis such as IR, ¹H NMR, and ¹³C NMR. The thermal behavior of the polysiloxane obtained was confirmed by DSC. In order to achieve the best possible yield and at the same time to get a polymer of high molecular mass, the operating conditions have been set at $t = 8$ h and $T = 70$ °C after the reaction was repeated several times. The average molecular mass and the polydispersity index were measured by GPC. A reaction mechanism has been suggested to show the action of the Maghnite-H⁺ during the reaction. Copyright © 2018 BCREC Group. All rights reserved

Keywords: Clay; Green catalyst; Maghnite-H⁺; Hexadecamethylcyclooctasiloxane; Polysiloxane

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1. Introduction

Chemistry suffers from a poor image tainted by old dogmas, basing on highlights of the industrial boom. Direct pollution of the atmosphere or the soil by uncontrolled releases of toxic effluents has contributed little to minimize

the popularization of this science which, nevertheless, is at the center of our society by its applications [1].

Green chemistry provides a framework for the prevention of pollution from chemical activities. The purpose of this environmentally beneficial chemistry is to design chemical products and processes to reduce, or eliminate the use and synthesis of hazardous substances. It also applies to the preparation of new products or greener processes through the search for alter-

* Corresponding Author.
E-mail: djamaledine.kherroub@yahoo.com (Kherroub, D.E.)
Telp.: +213-79-5565299 Fax.: +213-41-581413

native solutions, or the improvement of already existing approaches. This recent concept has been made popular, with the scientific community by the American chemists Paul Anastas, director of the Green Chemistry Institute in Washington, and John Warner, through publication in 1998 of the 12 principles of green chemistry which advocate the reduction, recycling or disposal of hazardous substances harmful for both man and the environment [2,3].

The development of new, clean and efficient processes for the preparation of heterogeneous catalysts developed is currently an important research axis in chemical synthesis. The term heterogeneous catalysis is used when the catalyst is solid, and the reactants are gaseous or in aqueous solution. The reactants and the catalyst do not evolve in the same phase. In heterogeneous catalysis, the surface of the solid catalyst in contact with the reactants plays a primordial role in the reaction. Indeed, it is at this level that the species react with one another, and are transformed to finally release the products of the reaction. The surface of the catalyst in contact with the reactants is called the active surface. A catalyst is more effective when its active surface is larger. Metals are widely used as solid heterogeneous catalysts, which are often toxic. Extensive studies are currently underway at several laboratories to design solid catalysts, which are less hazardous and more compatible with green chemistry principles. The alternative materials qualified to replace this type of catalyst are zeolites, mesoporous materials and especially clays.

In this study, Maghnite-H⁺ was used as a solid heterogeneous catalyst to synthesize polydimethylsiloxane (PDMS), from the polymerization of hexadecamethylcyclooctasiloxane (D8). Maghnite-H⁺ is obtained from an Algerian natural clay (research field of polymer chemistry laboratory at the University of Oran). After purification, treatment with sulfuric acid and proton intercalation, this clay leads to Maghnite-H⁺ [4,5]. The intercalation step associates the protons present in the acid with the sheets. This new catalyst was used to initiate the polymerization of various monomers [6,7], and also to synthesize different types of nanocomposites [8-10]. We are interested in the polymerization of D8 (Scheme 1a) by Maghnite-H⁺. The polymerization of siloxane monomers was carried out previously by different catalysts as phosphazene bases [11,12], strong bases [13,14], dodecylbenzenesulfonic acid [15], triflic acid [16], tris(pentafluorophenyl)borane [17] and trifluoromethanesulfonic acid [18].

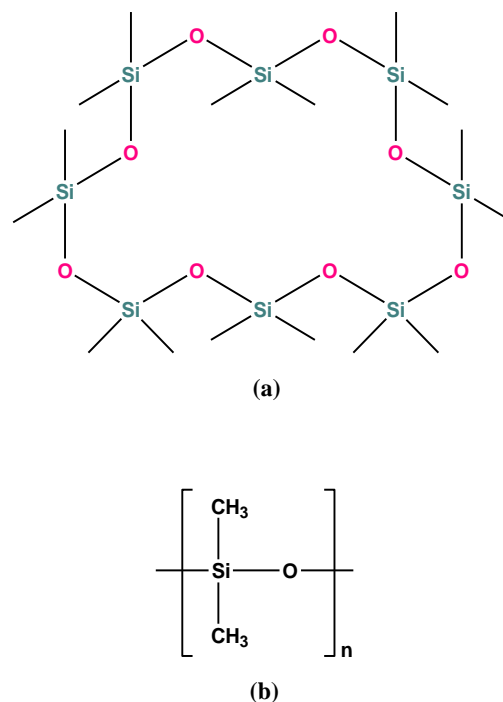
PDMS are organo-mineral polymers, characterized by the following molecular formula: (C₂H₆O₂Si)_n, n being the repetition number of the monomer (Scheme 1b) [19,20]. The covalent bonds which the silicon creates with the oxygen, to form the backbone of the macromolecules are exceptionally stable [21-24]. The simultaneous presence of organic groups attached to an inorganic backbone gives the PDMS; a unique combination of properties, and allows them to be used in a wide range of fields such as aerospace (performance at high and low temperatures), electronics (electrical insulation), healthcare (excellent biocompatibility) or in the construction industry (outstanding weatherability) [25-28], etc.

The objective of this work is to obtain polymers of polydimethylsiloxane type by replacing the conventional homogeneous catalysts with a new non-toxic heterogeneous catalyst prepared by simple activation of natural clay. The novelty of this method lies in the use of Maghnite-H⁺ (Algerian clay) for the polymerization of D8.

2. Materials and Methods

2.1 Materials

Hexadecamethylcyclooctasiloxane (D8, 98 %) was used as purchased from Aldrich chemical, without further purification. Methanol was purified by vacuum distillation. All other prod-



Scheme 1. The structure of (a) Hexadecamethylcyclooctasiloxane, and (b) Polydimethylsiloxane

ucts 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 was 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) was added, the stirring is continued for 48 h. After filtration and subsequent washing, the activated Maghnite was 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

A mass of 0.2 g of Maghnite-H⁺ was heated before use under vacuum with mechanical stirring for 30 min. The polymerization was carried in bulk. The dried amount of Maghnite-H⁺ was added to a flask containing 5 g of D8, the flask is immersed in an oil bath and brought to a temperature of 70 °C under reflux at 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 dried at 80 °C in vacuum for 6-8 h and weighed as polymer. Excess water was retrieved by evaporation at 105 °C; the amount of water necessary to stop the reaction would be then the difference between the initial amount and the recovered amount. 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 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 CuK α radiation ($\lambda = 0.154$ nm) at the rate of 5° min⁻¹ in the range of $2\theta = 2^\circ$ to 80°.

2.4.2 Infrared Spectroscopy

Infrared analysis of the polymers obtained was done using a Bruker Alpha FT-IR spec-

trometer equipped with an ATR accessory.

2.4.3 Nuclear Magnetic Resonance

The ¹H and ¹³C NMR spectrums 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 various thermal characteristic, 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.

2.4.5 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 polymethyl methacrylate of known molecular weight.

3. Results and Discussion

3.1 X-ray Diffraction (XRD)

Figure 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° (blue areas). Moreover, the acid treatment caused a shift of the peak of montmorillonite to small values of 2θ , from 8.41° to 5.73° , corresponding to an increase of the interlayer distance of montmorillonite (d_{001}) from 10.50 Å to 15.41 Å, this can be explained by the substitution of interlamellar cations of Maghnite by the hydronium ions (H₃O⁺) which have a larger atomic diameter.

3.2 Infrared Spectroscopy (IR)

Figure 2 provides the infrared spectra of the monomer and the obtained products for 4, 6, 8, 10, and 12 h at 70 °C. The broad peak seen at 3401 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 re-

leased proton of Maghnite-H⁺ and the oxygen atom at the end after the D8 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 2911 and 2858 cm⁻¹ are, respectively, due to C–H asymmetric/symmetric stretching of CH₃. The signal at 1272 cm⁻¹ is assigned to the CH₃ symmetric deformation of Si–CH₃. Peaks appearing at 1016 and 478 cm⁻¹ are respectively attributed to the stretching vibrations and deformation vibrations of the linear Si–O–Si structures. The signal at 797 cm⁻¹ is due to the Si–C stretching vibrations. The infrared spectrum of obtained PDMS using Maghnite-H⁺ as catalyst revealed no differences from those obtained by other researchers [29,30].

3.3 Proton Nuclear Magnetic Resonance (¹H NMR)

In order to identify more precisely the structure of the polymer obtained by the polymerization of D8 using the Maghnite-H⁺ 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 70 °C for 8 h. The results are shown in Figures 3a and 3b, which show the different chemical shifts. In both spectra, the dominant peak was observed at about 0.29 ppm, attributed to the methyl groups; it was more intense in the spectrum of the polymer meaning the large number of methyl groups in the polymeric chain. The small peak appearing at 4.98 ppm is assigned to the OH groups at the ends of polymer chains formed during the reaction. Similar results were obtained by Ramli *et al.* [31].

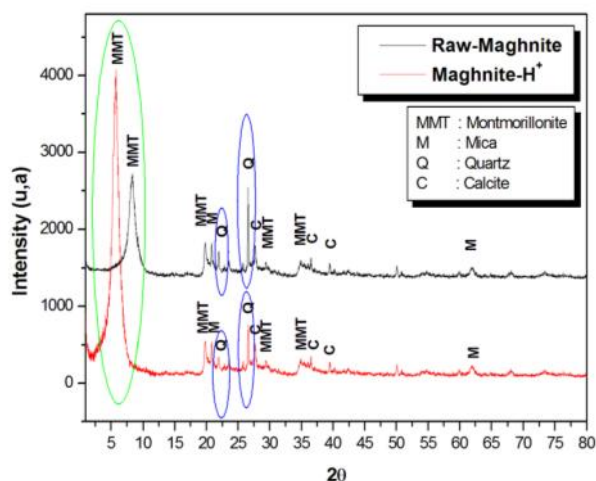


Figure 1. XRD patterns of the Maghnite before treatment (Raw-Maghnite) and after treatment (Maghnite-H⁺)

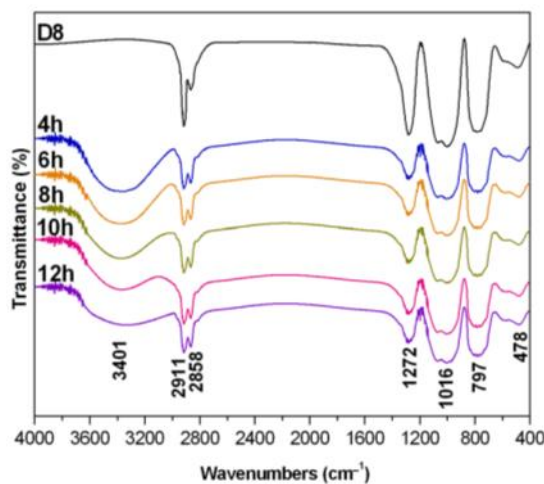
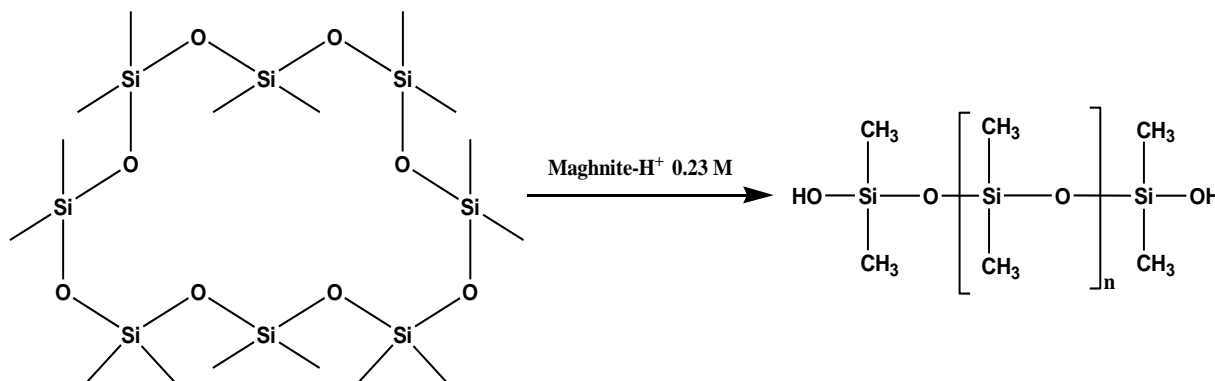


Figure 2. IR spectra of PDMS obtained by the polymerization of D8 at a temperature of 70 °C for different times



Scheme 2. Polymerization of D8 by Maghnite-H⁺

3.4 Carbon Nuclear Magnetic Resonance (¹³C NMR)

It was therefore necessary to analyze the products obtained by ¹³C NMR to provide a complement to the previous study. The results are shown in Figures 4a, 4b and 4c. The spectrum of the monomer was characterized by a single peak at approximately 0.12 ppm corresponding to the carbon of CH₃ (Figure 4a). The other two spectra correspond to ¹³C NMR spectrum of the polymer obtained after 8 h (Figure 4b) and the DEPT-135 spectrum of the polymer obtained after 10 h (Figure 4c). Both spectra have a characteristic peak at 0.2 ppm, which corresponds to methyl groups in the polymer chain. Moreover, there was the creation of a down peak at 32.61 ppm for the polymer obtained after 10 h, that is attributed to the carbon of CH₂, indicating the formation of ethylene bridges between linear polymer chains. These results showed that beyond 8 h of reaction time, the polymer chains could be crosslinked to form organopolysiloxane elastomers.

3.5 Differential Scanning Calorimetry (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, an exothermic peak and two endothermic peaks. The *T_g* was located at -120 °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 -48 and -40 °C, corresponding to the melting temperature, are 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 [32,33].

3.6 Effect of temperature

In an effort to understand and control more the polymerization reaction of D8 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 100 °C. The increase in temperature led to a significant increase in conversion reaching 96 % at 70 °C, beyond this temperature, this increase became negligible until the conversion stabilizes at its maximum at about 90 °C. On the other hand, the variation in average molecular mass shows two different behaviors, a gradual increase from 40 to 70 °C, followed by a reduction after just exceed its highest value at about 70 °C. We assume that it is the ceiling temperature, this decrease in average molecular mass can be explained by the fragmentation of the chains due to the 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 found in Table 1.

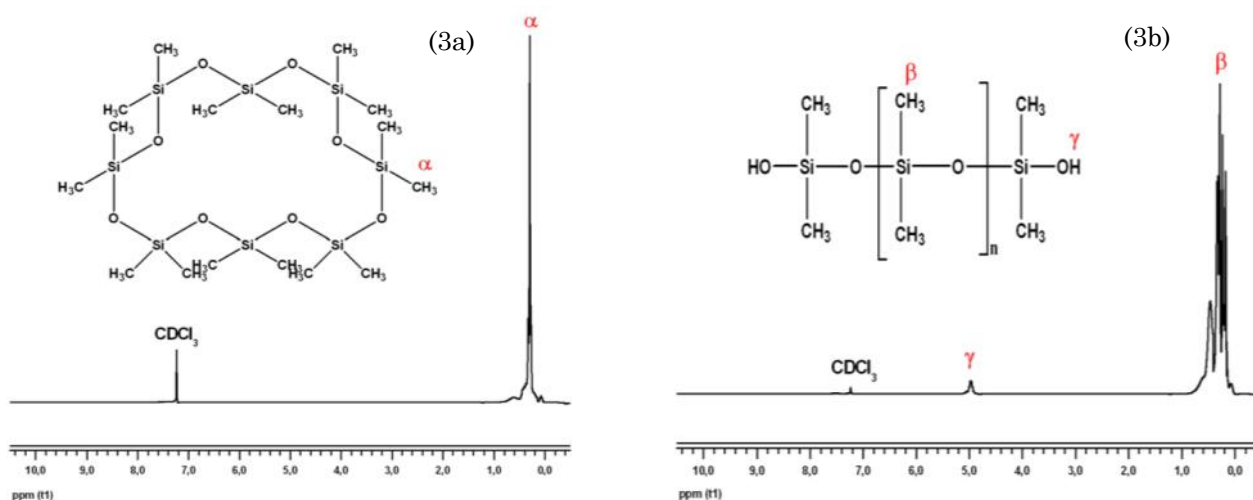


Figure 3. ¹H NMR spectra of D8 (a); ¹H NMR spectra of polymer obtained at a temperature of 70 °C for 8 h (b)

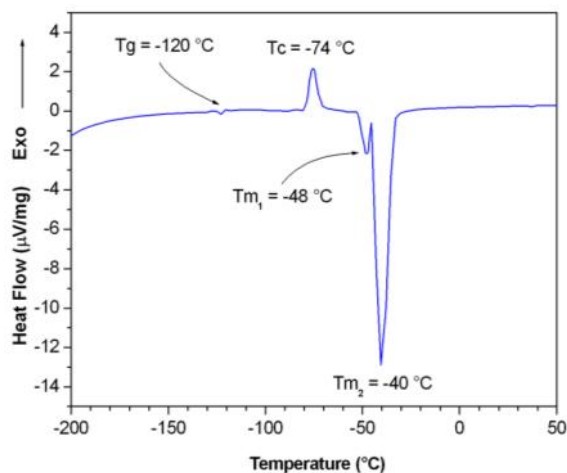
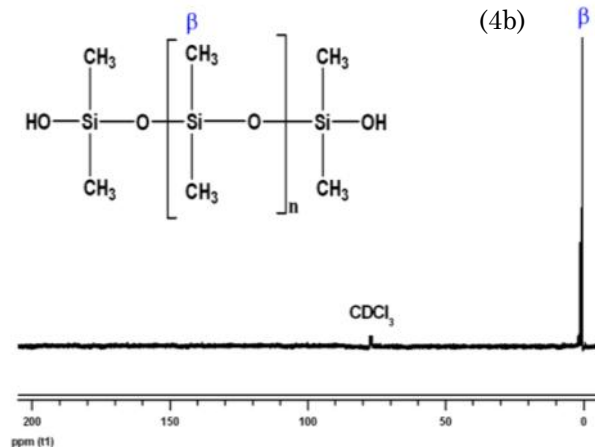
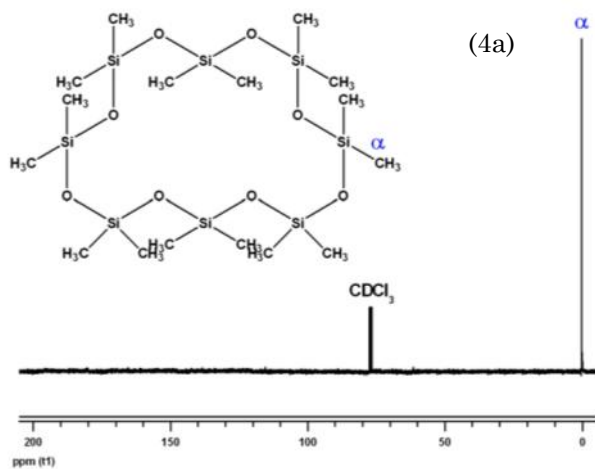


Figure 5. DSC thermogram of obtained PDMS

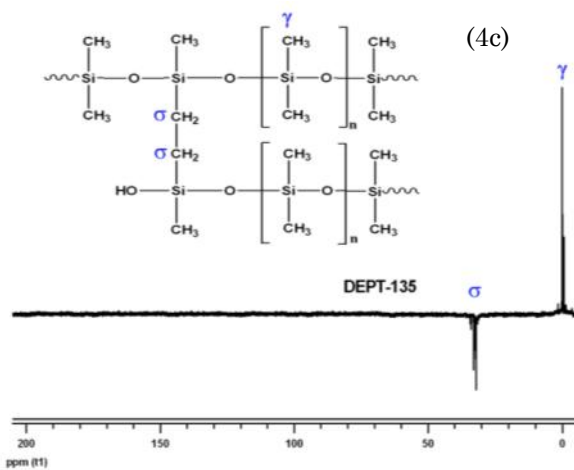


Figure 4. ¹³C NMR spectra of D8 (a); ¹³C NMR spectra of polymer obtained after 8 h at a temperature of 70 °C (b); and ¹³C NMR spectra of polymer obtained after 10 h at a temperature of 70 °C (c)

Table 1. Effect of reaction temperature on D8 polymerization^a

T (°C)	Conversion of monomer (wt %)	M_n	M_w/M_n
40	47	25807	1.11
50	63	66489	1.10
60	81	110888	1.14
70	96	167172	1.29
80	97	158021	1.31
90	98	98217	1.42
100	98	66749	1.47

^aMaghnite-H⁺/D8 weight ratio = 4 %. Reaction time 8 h.

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 D8, we performed the reaction with a catalyst content ranging from 2 to 6% 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 Figure 6 and 7, respectively. In all tests, the reaction was carried out in bulk and at a temperature of 70 °C. It is clearly noticeable that for all the different Maghnite-H⁺ contents, the reaction time had an effect proportionally positive on the monomer conversion before 10 h. After this duration, the effect of reaction time became 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 [34,35]. Moreover, the conversion of the monomer decreased when we used more than 4 % of the Maghnite H⁺, this is due to the existence of a large number of active sites carried on the surface of montmorillonite, which in turn began 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 increased with increasing reaction time, the maximum value for the different Maghnite-H⁺ contents was at 8 h, it is almost stabilized after that for 2 h, and

then began to decrease. The reduction over time, of the peak corresponding to OH groups exist only at the end of the polymer chains of PDMS synthesized by Maghnite-H⁺ was shown by the infrared analysis (Figure 2), it indicates that the chains became 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 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 ¹³C NMR analysis (Figure 4c). The decrease in the average molecular 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).

3.8 Kinetics and mechanism of the polymerization

In order to study the chemical kinetics of the polymerization reaction of D8 catalyzed 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 not the depolymerization phenomenon. The results clearly indicate that the reaction was first-order with respect to monomer (Figure 8). The linear approximation of experimental points allowed to calculate the reaction rate constant k using the equation: $\ln([D8]_t/[D8]_0) = kt$, where t is time of reaction [h], $[D8]_0$ is the initial D8 concentration and $[D8]_t$ is the D8 concentration at time t . Following this study, a reaction mechanism with several elementary steps was proposed, showing the role played by

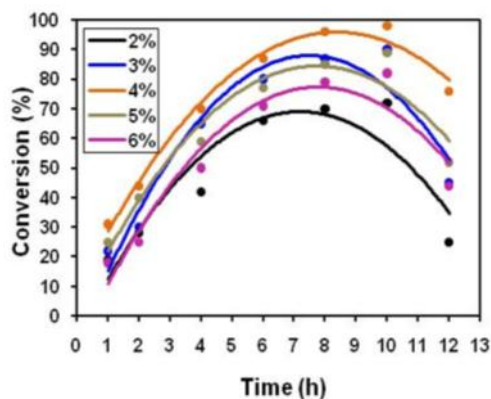


Figure 6. Effect of Maghnite-H⁺/D8 weight ratio on the conversion of monomer

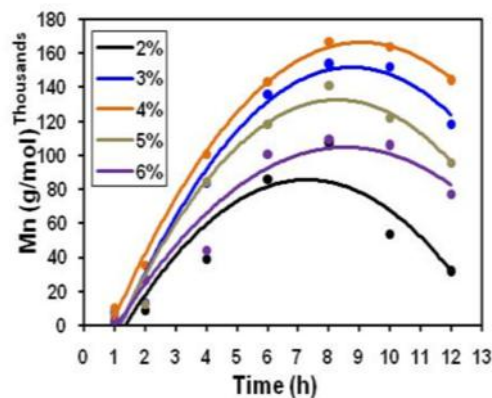


Figure 7. Effect of Maghnite-H⁺/D8 weight ratio on the average molecular mass

the Maghnite-H⁺ during each stage of this polymerization reaction (Scheme 3).

4. Conclusions

The modified Algerian clay (Maghnite-H⁺) showed from the results presented later, that it could be used as a green, ecological and cost-effective catalyst for polymerizing the hexadecamethylcyclooctasiloxane. The polymerization was carried out cationically by ring opening of the monomer, without solvent or diluents, and in the presence of a small effective amount of the catalyst (4 wt %). The initiation of the reaction was effectively ensured by the protons intercalated between the layers of the Maghnite-H⁺.

The advantage of this heterogeneous catalyst, proposed as an alternative to the strong acids used previously, was to achieve relatively high yields by obtaining at the same time polymers of linear structure. The reaction took place under mild conditions in order to design a modern procedure, while respecting the principles of green chemistry.

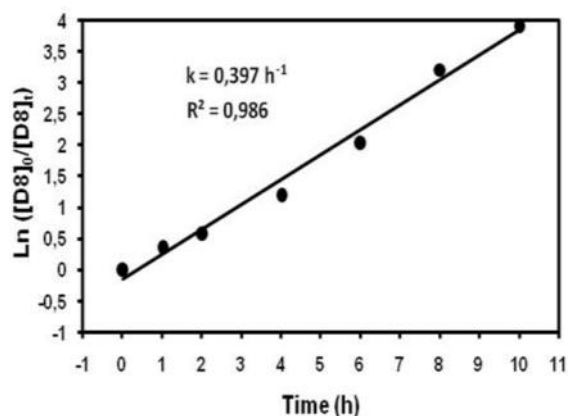


Figure 8. Effect of Maghnite-H⁺/D8 weight ratio on the conversion of monomer

The characterization methods (IR, ¹H NMR, ¹³C NMR and DSC) showed no difference either in the molecular structure, or in the thermal properties of the PDMS obtained compared to those obtained subsequently by other catalysts. The evolution of the average molecular mass, and the polydispersity index as a function of the operating conditions were followed by GPC, the best result was obtained at t = 8 h, T = 70 °C and Maghnite-H⁺/ D8 weight ratio = 4 %.

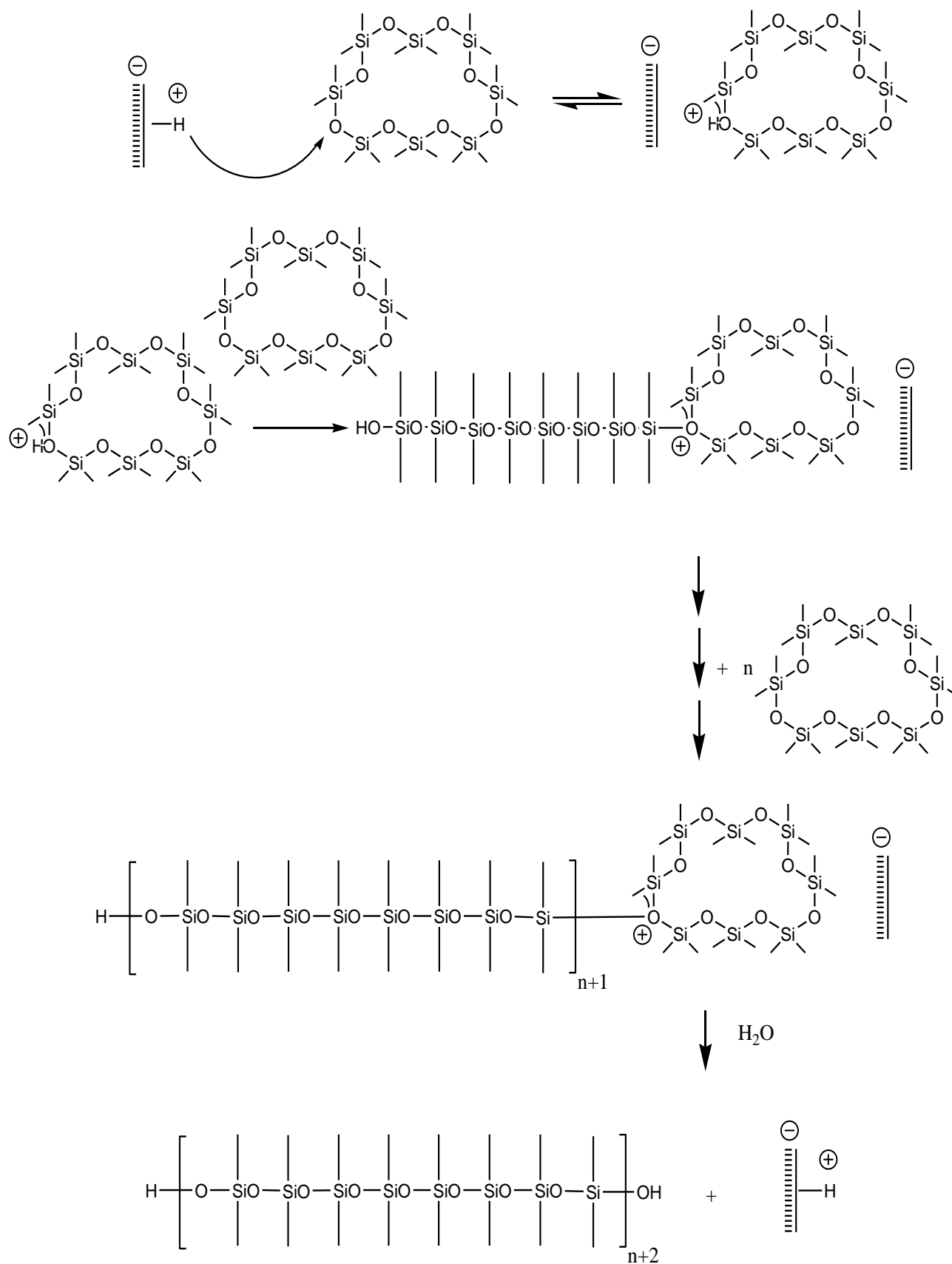
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Table 2. Kinetic evolution of D8 polymerization^a initiated by Maghnite-H⁺

Time (h)	Conversion of Monomer (wt %)	M_n	M_w/M_n
1	31	9890	1.08
2	44	35214	1.11
4	70	101012	1.19
6	87	143247	1.20
8	96	167172	1.29
10	98	164248	1.39
12	76	144555	1.43

^aMaghnite-H⁺/ D8 weight ratio = 4%. Reaction temperature 70 °C



Scheme 3. Mechanism of D8 Polymerization catalyzed by Maghnite-H⁺

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