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Green Synthesis of Copolymer Electrolytes for Lithium Batteries Catalyzed by an Ecocatalyst Maghnite-H$^+$

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ABSTRACT

The ideal electrolyte material for a solid-state battery would have the ionic conductivity of a liquid, the mechanical properties of a solid, and the formability of a commodity thermoplastic. The ionic conductivity changed with the molecular weight of the polymer, it varies inversely with the glass transition temperature. In our study, to achieve high ionic conductivity, we synthesize copolymer PDMS/PEO as polymer electrolytes by a simple method, one step of catalytic ring opening polymerization using Maghnite-H$^+$ (Mag-H$^+$), a montmorillonite sheet silicate clay exchanged with protons. It is preferred for its many advantages: a very low purchase price compared to other catalysts, the easy removal of the reaction mixture. The reaction of copolymerization is carried out in chloroform at 60°C for 10 h. POE used is POE 400 and POE 1000. PDMS with a Tg of -123°C was synthesized. Various techniques, including 1H-NMR, IR, DSC, XRD and TGA were used to elucidate structural characteristics and thermal properties of catalyst and products. Analyses results confirm the synthesis of the copolymer (PDMS / PEO) with different percentage composition of each polymer. Cationic mechanism for the reaction was proposed.

Keywords: Cationic ring opening polymerization; PDMS-co-PEO; Ecological catalyst; Maghnite-H$^+$; Polymer electrolyte

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INTRODUCTION

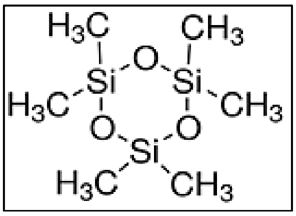
The lithium solid polymer electrolyte battery is arguably the most attractive technology for rechargeable electric power sources, boasting the highest predicted energy density, the fewest environmental, safety, and health hazards, low projected materials and processing costs, and the greatest freedom in battery configuration [1-3]. It is widely recognized that solid polymer electrolytes can be potentially applied in many solid electrochemical devices such as high-energy density batteries, electro chromic windows, and light-emitting devices [4,5]. The polymer electrolytes to be used in the devices have to satisfy several requirements, including high ionic conductivity, electrochemical stability, and good mechanical properties [4,6-9]. For nearly 20 years, poly (ethylene oxide)-based materials have been researched for use as electrolytes in solid-state rechargeable lithium batteries. Poly(ethylene oxide) (PEO) is currently the most prominent example of a polymer electrolyte due to its ability to solvate and transport lithium-ions. Technical obstacles to commercialization derive from the inability to satisfy simultaneously the electrical and mechanical performance requirements: high ionic conductivity along with resistance to flow [1]. Poly(ethylene oxide) (PEO) and its derivatives have been used as matrix polymers in most of studies of polymer electrolytes, since PEO contains ether coordination sites, which assist the dissociation of salts incorporated in the polymer, as well as a flexible macromolecular structure, which promotes facile ionic transport [4]. Although PEO-salt complexes are highly conductive at high temperatures (> 10^{-4} S cm^{-1} at 70°C), these same materials lose their conductivity rapidly upon crystallization (Tm 65°C for PEO) [1]. However, PEO-based polymer electrolytes show comparatively low ionic conductivity at ambient temperatures. The reasons for the low ionic conductivity are (a) the existence of crystalline domains, which interfere with the ionic transport, and (b) the dependence of the ionic transport on main-chain segmental motions which rapidly diminish with decreasing temperature [4]. Given the phenomenological relation between ionic conductivity and chain mobility, research has been directed toward synthesizing amorphous, low-Tg polymer electrolytes. Strategies to improve conductivity at ambient temperatures include modified molecular architectures and compositions to preempt crystallization. These approaches have resulted in materials with high conductivities at ambient temperatures [10]. A variety of block copolymers using EO have been synthesized and studied as electrolytes. Typically, the ionic conduction is ensured by one or more blocks of PEO and mechanical strength is provided by a block of a different nature [11,12]. The ideal material for electrolytes should have the ionic conductivity of a liquid, the mechanical properties of a solid, and the forming ability of thermoplastic material [13]. The electric conductivity varies inversely with the glass transition temperature [9], the mobility of the polymer chain is recommended for the conduction of Li+ [13]. PDMS has low glass transition temperature (Tg) and excellent chemical constancy. Polymer electrolytes incorporating polysiloxane and PEO segments were fabricated to achieve satisfactory process ability and high ionic conductivity. Furthermore, it has been reported that PDMS segments tend to segregate the other rest organic moieties due to its low surface energy and poor miscibility [14]. Thermal stability of the polymer electrolyte, at a temperature higher than the lithium melting point (Tm + 180°C) gives great safety in case of a short-circuit. As regards the mechanical properties, by lowering the polymer thickness, they allow the ohmic drop to be decreased and these batteries to be used commonly between 50 to 80°C without damage. This is required for electrical car application [15].

PDMS has a Tg of -123°C and a flexible and movable chain. The rotation around the axis Si-O is very easy. View of these properties, the PDMS was chosen in the synthesis of electrolyte to increase it conductivity. PDMS was an attractive candidate, expected to impart conductivities higher than previously attained [14]. In the present work, Algerian Montmorillonite (an ecocatalyst) was used to prepare copolymer PDMS-PEO. An insoluble acidic catalyst is excellent option for environmentally friendly polymerization route.

EXPERIMENTAL SECTION

Materials

Hexamethylcyclotrisiloxane (D3), Polyethylene glycol and chloroform were purchased from Sigma Aldrich and used as received. Raw-Maghnite: Algerian montmorillonite clay which has been used to prepare Maghnite-H^+, comes from a quarry located in Maghnia (North West of Algeria) and was supplied by company “ENOF” (Algerian manufacture specialized in the production of non-ferric products and useful substances).



Scheme 1: Strurture formula of hexamethylcyclotrisiloxane

Preparation of Montmorillonite -H^+

Maghnite-H^+ was prepared by a method similar to that described by Yahiaoui et al. [16]. The raw Maghnite is activated with a sulfuric acid solution to give a Maghnite exchanged with protons, called Mag-H^+. In an Erlenmeyer flask, crushed raw Maghnite (30 g) was dispersed in a volume of distilled water (120 ml). The mixture was stirred using a magnetic stirrer for 2 h at room temperature. Then, a solution of sulfuric acid 0.5 M (100 ml) was added. The solution thus obtained was maintained for two days under stirring. The mineral was filtered off and washed several times with distilled water up to pH 7. After filtration, the Mag-H^+ was dried in an oven for 24 h, at 105°C and was then crushed. The catalyst structure was found by X-ray diffraction (Figure 1).

Synthesis of PDMS and PDMS-co-PEO

PDMS was synthesized by ring-opening polymerization of D_3 in chloroform at 60°C for 8h. Addition of catalyst (Maghnite-H^+) to the mechanical stirred solution containing D_3 and solvent is 6% by mass. Before use, Mg-H^+ was dried in an oven at 120°C overnight. PDMS obtained has Tg of -124°C, which promotes its use as conductor. PDMS-co-PEO copolymer was synthesized by cationic ring opening polymerization; the reaction is catalyzed by the Maghnite-H^+ (8%). The structural parameters we varied are the molecular weight of PEO and the proportion of (PDMS / PEO) and (D_3 / PEO). This copolymerization is carried out in chloroform at 60°C, by two routes of synthesis: From PDMS + PEO, or directly from PEO and the monomer (D_3), according to reactions shown in Scheme 1. Regarding the copolymerization of PDMS + PEO, the two polymers are introduced into the reaction at the same time; while when using the monomer, the latter is stirred magnetically with the catalyst in chloroform for 2 h after this time the PEO is added. The reaction in both cases lasts 24 hours. To purify the resulting copolymer, a mixture of (chloroform + water) is added to the filtrate of the copolymerization reaction in a separating funnel. Two phases are separated; the operation is repeated several times. The lower phase (chloroform) was evaporated in a rotary evaporator. The recovered copolymer was dried and weighed (Figure 2). Polyoxyethylene methacrylate polydimethyl siloxane (POEM - PDMS) electrolytes have been synthesized by radical polymerization by Patrick E et al. [17].

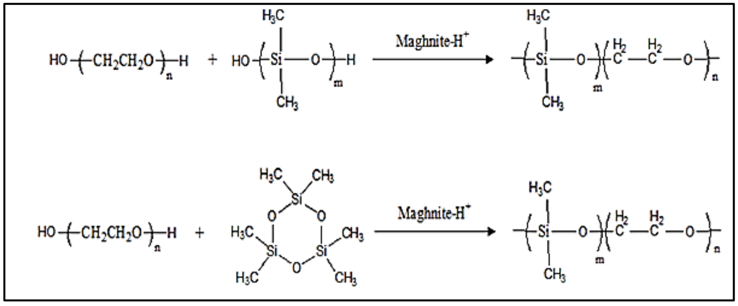


Figure 1: Scheme of synthesis of PDMS-co-PEO

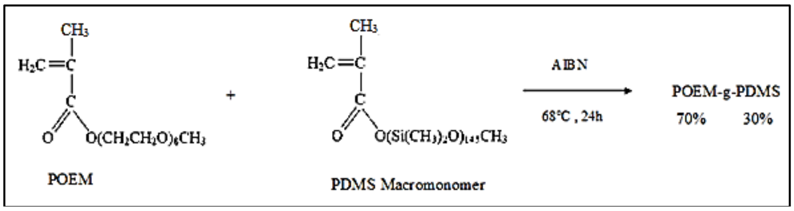


Figure 2: Scheme of synthesis of POEM-g-PDMS

RESULTS AND DISCUSSION

Structural Analyses

The chemical structure of the products was determined by:

^{1}H nuclear magnetic resonance (NMR) measurements, carried out on a 300 MHz avance Bruker NMR Spectrometer. Fourier transforms infrared spectroscopy (FTIR) analyses, obtained between 900 and 4000 cm^{-1} on FT-IR-Spectroscopy Alpha-P ATR Bruker. The TGA curves were recorded using a thermogravimetric instrument Type TGA Q500 V6.4 Build 193. X-ray diffraction (XRD) (Figure 3), for Mag-H$^+$, obtained on D8 Advance Bruker AXS X-ray diffractometer. DSC measurements, carried out on Netzsch DSC 204 F1 Phonix 240-12-010-L, according to the following program: the specimens were heated at a rate of 10°C /min from -140°C to 30°C.

Characterization of Maghnite-H$^+$

The difference between raw Maghnite and Maghnite-H$^+$ is in the basal spacing (d_{001}), which is calculated from XRD patterns, applying Bragg equation ($2d\sin\theta = n\cdot\lambda$).

d_{001} raw Maghnite = 11.45 Å, d_{001} Maghnite-H$^+$ = 15.5 Å (Figure 2).

The thermal characterizations of Magh-H$^+$ include thermogravimetric analysis (TGA). Figure 4 shows the weight losses (%) versus temperature (°C) curves for pure Maghnite-H$^+$. TGA of pure Maghnite-H$^+$ shows three stages of weight loss. The first weight loss in Mag-H$^+$ below 200°C is a result of the loss of water to the interleaved surface. The second weight loss around 500°C corresponds to the loss in residual water. Beyond 500°C is associated with the dehydroxylation of silicate structure.

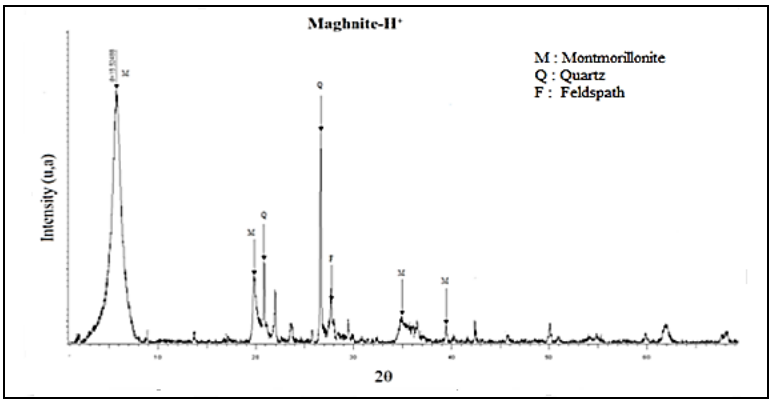


Figure 3: XRD patterns of the clay (Mag-H+)

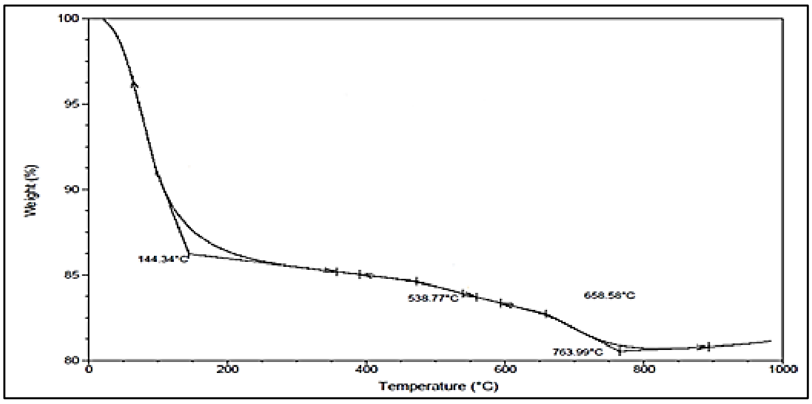


Figure 4: TGA curves of a Maghnite–H+ obtained in nitrogen atmosphere at heating rate of 10°C/min

Characterization of Products

The aim of this research is the synthesis of a copolymer used as electrolyte in lithium-polymer battery, by one step; using an ecological, economic and especially a very efficient catalyst in the ring opening polymerization.

The FTIR spectrum of copolymer (PDMS-co-PEO) is shown in Figure 5, the bands characteristic of polydimethylsiloxane were observed. Vibration modes involving only the methyl groups: the stretching modes θ (CH) formed a whole between 2905 and 2962 cm^{-1}, while the vibration modes corresponding to the deformation δ (CH_3) were centered at 1414 cm^{-1}. Modes elongation θ (SiOSi) in the form of an intense peak accompanied by a shouldering appeared between 1008 and 1078 cm^{-1}. Absorption bands involving Si-C bonds with an intense band is observed at 789 cm^{-1} due to the deformation (rocking) Si-CH_3. Stretching band at 868 cm^{-1} and a significant band at 1258 cm^{-1} corresponding to a vibration C-C (bending). The C-C-O bonds are determined at 1083 cm^{-1}. The C-OH bond is observed at 1257 cm^{-1} and terminal OH group at 3430 cm^{-1}. In order to accurately characterize the microstructure of each copolymers (proportion of each block), H^1 NMR analyzes were performed. NMR spectra obtained for the copolymers PDMS / PEO are shown in Figures 6 and 7. The peaks at 0 ppm denote CH_3 of PDMS; the peaks at 3.2-3.8 denote CH_2 of PEO the same results were obtained by Dae-Won Chung et al. [18]. ^{1}H NMR and IR spectra confirmed the synthesis of PDMS-PEO copolymer.

In NMR spectrum of PEO, the peak corresponding to OH group appears after the peak of the two CH_2 groups of repeat unit, the thing that is reversed in our spectrum. This is explained by the attractor effect of Si-O of the OH group, confirming that the synthesized product is the copolymer PDMS-co-PEO. A thermogram of PDMS is represented in Figure 8. It has been shown that high molar mass linear PDMS polymers are highly crystalline and show an exothermal crystalline formation (cold crystallization T_c) and an additional crystallization exotherm; (T_c^*) situated just between the two melting peaks; (T_{m1} and T_{m2}) in overall agreement with literature values [19,20]. The two melting peaks correspond to two different types of crystals. It is considered that the cold crystallization corresponds to a recrystallization of metastable crystals, which finally melt at the higher melting temperature T_{m2} while the peak at T_{m2} corresponded to the melt of the less perfect crystals formed during cooling. Glass transition (Tg) is found at -124°C, knowing that the electrical conductivity varies inversely with the glass transition temperature, which promotes the PDMS to be used in electrolytes.

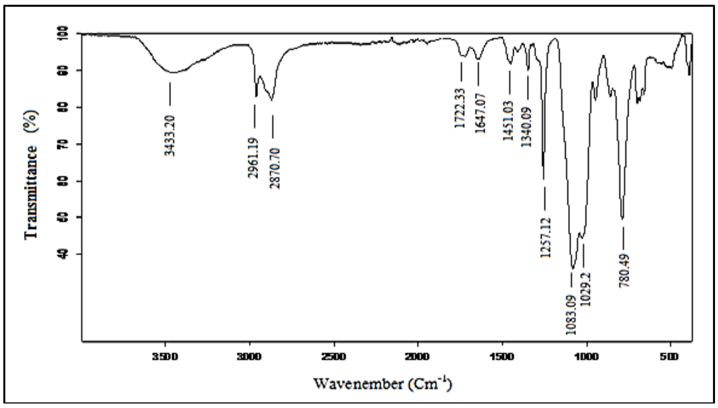


Figure 5: FTIR Spectra of copolymer (PDMS-PEO)

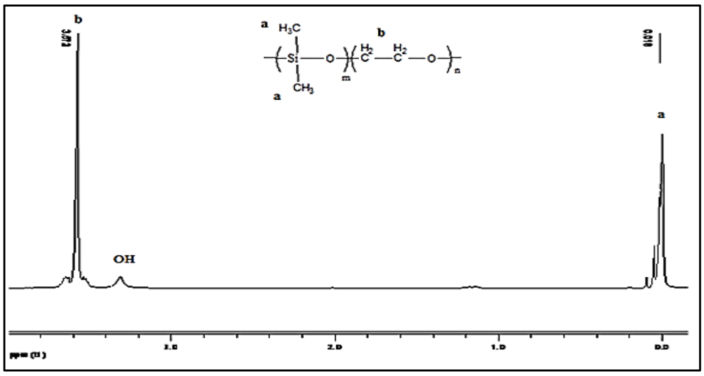


Figure 6: ^{1}H-NMR spectrum of copolymer (PDMS-PEO) (initial weight ratio D3/PEO (20/1)

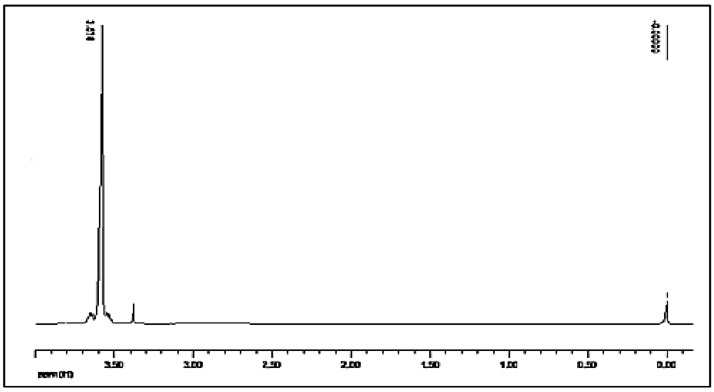


Figure 7: ^{1}H-NMR spectrum of copolymer (PDMS-PEO) (initial weight ratio PDMS/PEO: 1/1/)

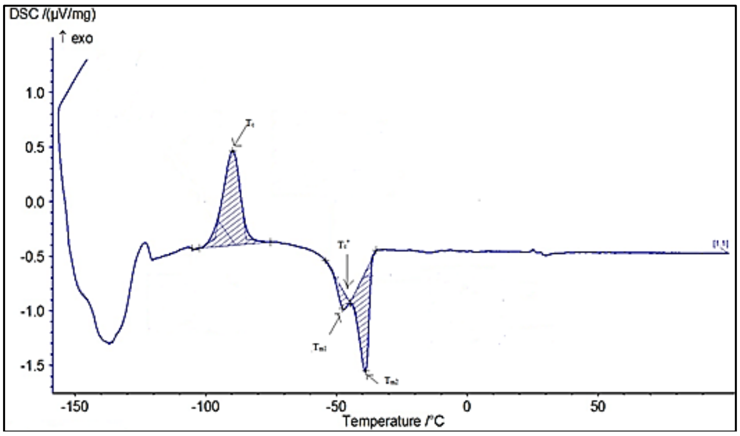


Figure 8: DSC thermogram of PDMS obtained at a heating rate of 10°C min^{-1}, cooling rate 10°C min^{-1}

Calculation of Chemical Composition of the Copolymers Obtained

Chemical composition of the copolymers was determined from the peak area of NMR spectrum. Summarizes the chemical composition of PDMS / PEO copolymers synthesized. Calculations are performed using the following method: A1 and A2 the integrals of the NMR peaks at 0 and 3.2-3.8 ppm respectively, X and Y the number of PDMS and PEO repeating unit respectively. M1, M2 the corresponding masses of PDMS and PEO repeating unit. A1 is the area of methyl protons of PDMS (6X protons)

A2 is the area of CH_2 protons of the PEO (4Y protons).

We can deduce:

A1=6X ⇒ X=A1/6 A2=4Z ⇒ Z=A2/4

The proportions of each block are defined as follows:

% PDMS = M1/ (M1+M2) avec M1 = 74X % PEO = M2/(M1+ M2) avec M2 = 44Y

We deduce the following equations:

$$\% \text{ PDMS} = \frac{\frac{74}{6}\text{A1}}{\frac{74}{6}\text{A1}+\frac{44}{4}\text{A2}} \quad \% \text{ PEO} = \frac{\frac{58}{4}\text{A1}}{\frac{74}{6}\text{A1}+\frac{44}{4}\text{A2}}$$

According to the results of Figures 9-11, PDMS-co-PEO copolymers can be synthesized with different percentage composition of each polymer, depending on the conditions of use of this copolymer as electrolyte.

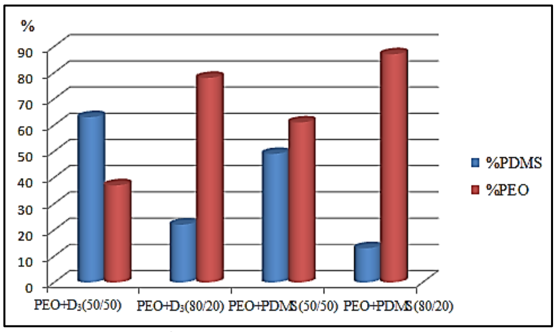


Figure 9: Chemical composition of the copolymers (PDMS-PEO) synthesized from PEO 400

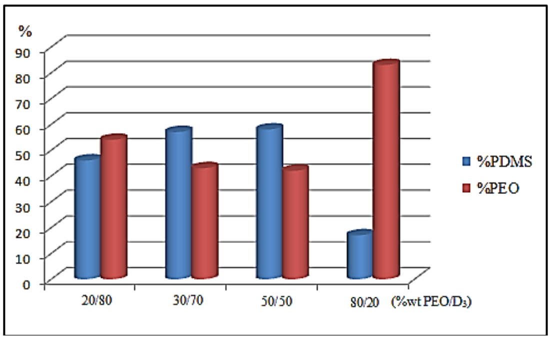


Figure 10: Chemical composition of the copolymers (PDMS-PEO) synthesized from PEO1000 + D3

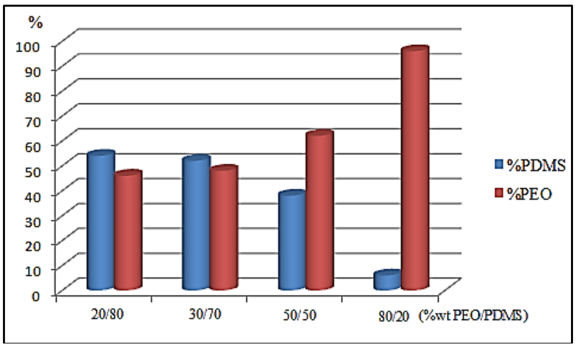


Figure 11: Chemical composition of the copolymers (PDMS-PEO) synthesized from PEO 1000 + PDMS

Mechanism of Copolymerization

Copolymerization mechanism is proposed in Figure 12.

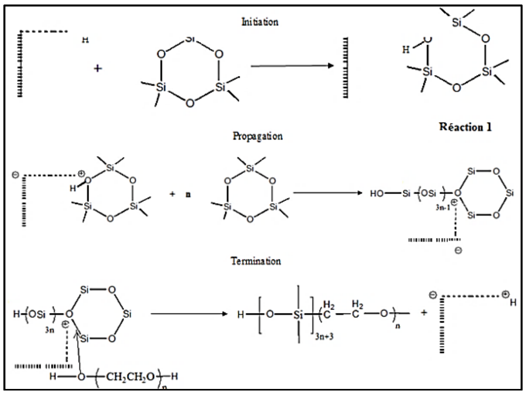


Figure 12: Mechanism of copolymerization PDMS-PEO

CONCLUSION

The efficiency of clay (Maghnite-H^+) prepared and used us an ecological catalyst was confirmed. we have succeeded the cationic ring opening polymerization of Polydimethylsiloxane with polyethylene oxide. PDMS-PEO copolymers were synthesized in solution at 60°C. FTIR spectrum confirmed the existence of characteristic bands corresponding to PDMS and PEO in the synthesized copolymer. H^1 NMR spectrum confirmed the structure of the copolymers. The chemical composition of the copolymers was determined from NMR peaks integral. It was demonstrated that chemical composition of copolymers depends on the ratio of D_3 /PEO. Application of copolymer PDMS-PEO in Lithium-Polymer Batteries will be a subject of our investigations in the future.

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