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Green Synthesis of copolymer (PDMS-co-PEO) Catalyzed by an ecocatalyst Maghnite-H+

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ABSTRACT

Since the discovery of ionic conduction properties of polyethylene oxide doped with lithium, the researchers looked for a material having conductivity suitable for separating the electrodes. The electric conductivity varies inversely with the glass transition temperature, the mobility of the polymer chain is recommended for the conduction of Li^+. PDMS has a Tg of -123°C, a flexible and mobile chain. View of these properties, the PDMS was chosen in the synthesis of electrolyte to increase it conductivity.

The present study shows the synthesis copolymer PDMS-co-PEO by a simple method, one step of catalytic ring opening polymerization using Maghnite-H^+ (Mag-H^+), a montmorillonite sheet silicate clay exchanged with protons, an efficient catalyst for cationic polymerisation of many heterocyclic. The reaction of copolymerization is carried out in chloroform at 60°C for 10h. Various techniques, including ^{1}H-NMR, IR, DSC, XRD and TGA were used to elucidate structural characteristics and thermal properties of catalyst and products.

Analyses results confirms the synthesis of the copolymer PDMS / PEO, cationic mechanism for the reaction was proposed.

Keywords: Cationic Ring Opening Polymerization; PDMS-co-PEO; Ecological Catalyst; Maghnite-H^+; Polymer electrolyte; ^{1}H-NMR.

INTRODUCTION

The development of lithium batteries has gained an unprecedented significance in the last two decades as the demand for portable telecommunication devices, computers and eventually hybrid electric vehicles has been an ever-increasing one [1,2].

The advantages such as no-leakage of electrolyte, higher energy density, flexible geometry and improved safety hazards have drawn the attention of many researchers on the development of lithium polymer batteries [3].

Poly(ethyleneoxide) (PEO) was the earliest and extensively studied system. Although, the ionic conduction of PEO was discovered by Fenton et al. [4] in 1973, its technological importance was recognized only in the early of 1980 [5].

Since the discovery of the ion-conducting properties of doped polyethylene oxide, researchers have searched for a material exhibiting liquid-like ionic conductivity and mechanical properties suitable for separating the electrodes [6-10].

However, these electrolytes offered very low ionic conductivity. Works have focused on block copolymer electrolytes. Alloin [11] Nishimoto [12] prepared by ring-opening polymerization (ROP) copolymers based EO units and of a crosslinkable comonomer. With these materials, they found a significant decrease in the crystalline phase of PEO and measured very interesting conductivities in the range of 10^{-4} $S.Cm^{-1}$ at room temperature.

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 [13].

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.

The electric conductivity varies inversely with the glass transition temperature [10], the mobility of the polymer chain is recommended for the conduction of Li + [14].

Polyorganosiloxane have a chemical structure based on alternating silicon atoms and oxygen.

Covalent bonds that create the silicon with oxygen to form the backbone of the macromolecules are exceptionally stable. This leads for polydimethylsiloxane (PDMS) to high temperature resistance.

The high valence angle of the Si-O-Si, high distance interatomic Si-O and no substituent on the oxygen atom; leads to a flexible and movable chain. The rotation around the axis Si-O is very easy [15].

The rotation barriers are low and the siloxane chain can adopt many conformations. The energy of rotation about a bond $CH_2 - CH_2$ of polyethylene is 13.8 kJ/mol, but only 3.3 kJ/mol around a bond $(CH_3)_2$ Si - O, corresponding to an almost free rotation (Figure 1).

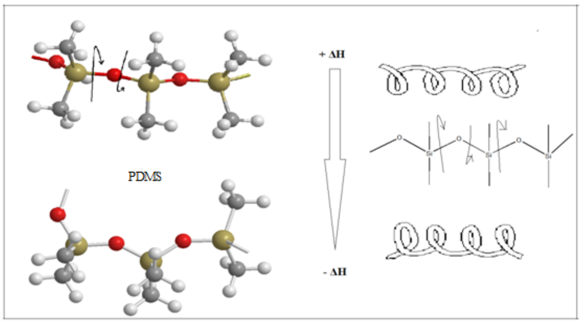


Figure 1. PDMS Rotation.

The silicones modified with hydrophilic poly (ethylene oxide) (PEO) are widely used in many industrial fields due to their unique combination of properties [16]. Copolymers Silicone -PEO have a strong tendency to provide maximum benefits at low concentrations. The differences in their physical properties have been well summarized in the literature.

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 [17].

MATERIALS AND METHODS

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).

Preparation of Montmorillonite –H^+

Maghnite-H^+ was prepared by a method similar to that described by Yahiaoui et al (18). 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 2**)**.

Catalyst structure

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

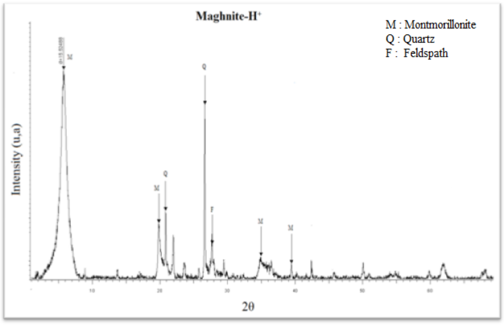


Figure 2. XRD patterns of the clay (Mag-H^+).

The IR spectra of montmorillonite were studied by many authors, Farmer [19] Abdelouahab et al. [20] and John, Hiser and Karr [21]. From this work we can identify the spectrum of natural clay in Figure 3:

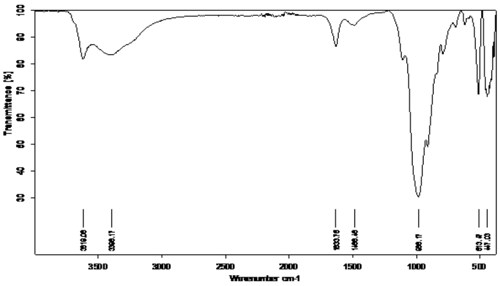


Figure 3. FT- IR spectrum of the Maghnite-H^+.

- Two bands of adsorption located in 3619 and 3396 cm^{-1} respectively are due to vibration of the OH groups of the silicate skeleton constitution and OH physisorbed by clay.

- The band at 1633 cm^{-1} is attributed to the angular deformation of adsorbed water molecules between the sheets

- The presence of absorption band between 900 and 1100 cm^{-1}, centered at 1000 cm^{-1} characteristic of the Si -O. Some authors attribute the movement of this band to lower frequencies, on the one hand to the presence in substantial amount in tetrahedral site trivalent ions of silicon substituted and secondly to the presence in the octahedral site of ferric ions disrupting Si-O vibrations.

- At 513 cm^{-1}, a vibration band is observed, attributed to deformation of the Al -O bond.

- Vibration M*-O-H (M * Metal position in octahedral Al, Mg, Fe, Li), manifested by a peak at 914 cm -1

The thermal characterizations of the composites include thermogravimetric analysis (TGA). Figure 4 shows the weight losses (%) versus temperature (°C) curves for pure Maghnite-H^+. The 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.

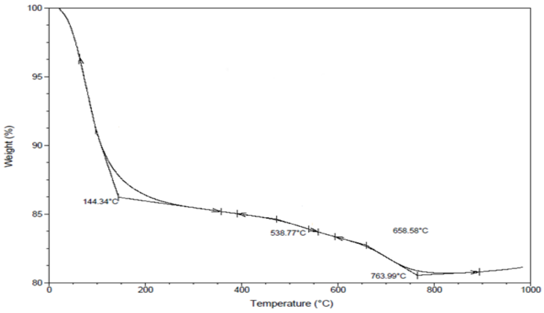


Figure 4. TGA curves of a Maghnite–H^+ obtained in nitrogen atmosphere at heating rate of 10 °C/min.

Synthesis of product

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.

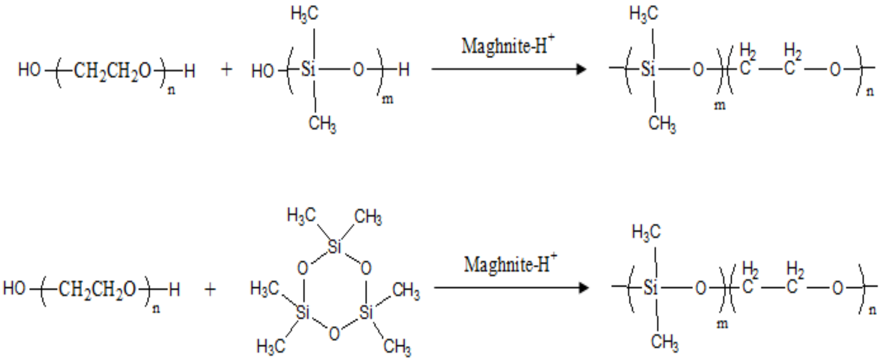
PDMS obtained, has Tg of -124°C, which promotes its use as conductor.

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 Scheme1.



Scheme 1. Synthesis of PDMS-co-PEO.

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 (Scheme 1).

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 transform 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) 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 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) $Si\text{-}CH_3$.

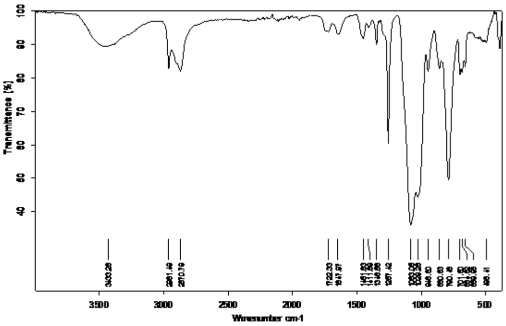


Figure 5. FTIR Spectra of copolymer (PDMS-PEO).

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 $C\underline{H}_3$ of PDMS, the peaks at 3.2-3.8 denote $C\underline{H}_2$ of PEO

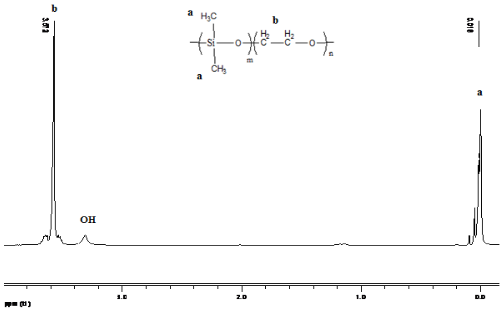


Figure 6. 1H-NMR spectrum of copolymer (PDMS-PEO) (initial weight ratio D3/PEO : 20/1).

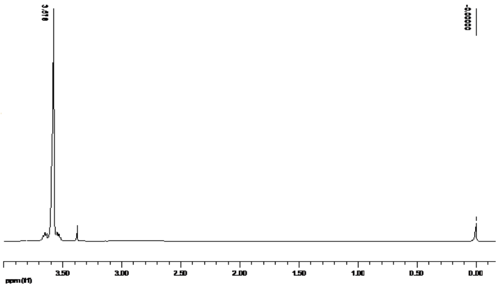


Figure 7. 1H-NMR spectrum of copolymer (PDMS-PEO) (initial weight ratio PDMS/PEO: 1/1/).

The same results were obtained by Dae-Won Chung et al. [22].

1H 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 [23,24].

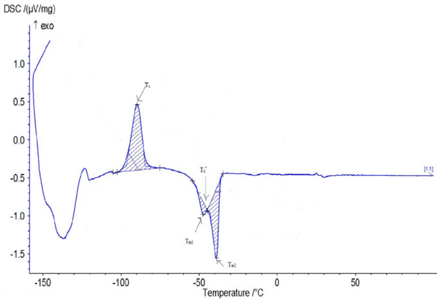


Figure 8. DSC thermogram of PDMS obtained at a heating rate of 10°C min^{-1}, cooling rate 10°C min^{-1}.

The two melting peaks correspond to two different type 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, as schown in Figure 8.

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.

Calculation of chemical composition of the copolymers obtained

Chemical composition of the copolymers was determined from the peak area of NMR spectrum. Table 1, summarizes the chemical composition of PDMS / PEO copolymers synthesized. Calculations are performed using the following method:

Table 1. Chemical composition of the copolymers (PDMS-PEO) synthesized

Molar Mass PE O g.mol^{-1}	PDMS(%wt)	PE O (%wt)	D3(%wt)	Copolymer Composition (%PDMS/%PE O)
400		50	50	63/37
400		80	20	22/78
400	50	50		49/51
400	20	80		13/87
1000		80	20	17/83
1000		50	50	58/42
1000		30	70	57/43
1000		20	80	46/54
1000	20	80		6/96
1000	50	50		38/62
1000	70	30		52/48
1000	80	20		54/46

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

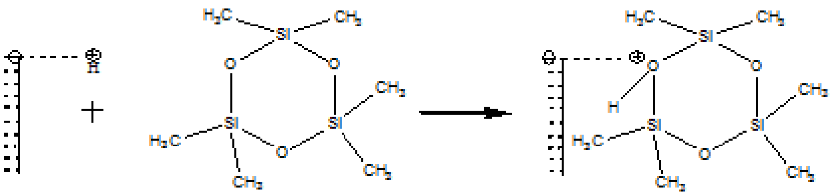
We deduce the following equations:

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

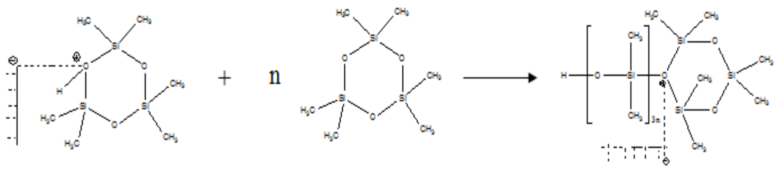
According to the results of Table 1, PDMS-co-PEO copolymers can be synthesized with different percentage composition of each polymer, depending on the conditions of use of this copolymer as electrolyte.

Mechanism of Copolymerization

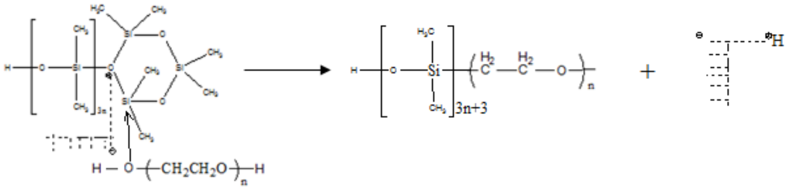
Schemes 2-4



Scheme 2 : Initiation.



Scheme 3 : Propagation.



Scheme 4 : Termination.

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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