Chemistry

GREEN SYNTHESIS OF FUNCTIONALIZED POLY(3-GLYCIDOXYPROPYL-TRIMETHOXYSILANE) USING AN ECO-CATALYST (TREATED MONTMORILLONITE)

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Abstract. Telechelic poly(3-glycidoxypropyltrimethoxysilane) (PGPTMS) with acetate and methacrylate end groups was successfully synthesized by an efficient and solvent-free approach, with anhydrides (acetic anhydride (AA) and methacrylic anhydride (MA)), by cationic ring-opening polymerization of 3-glycidoxypropyltrimethoxysilane (GPTMS), using an ecologic solid catalyst Maghnite-H$^+$ (Mag-H$^+$), instead of electrophilic catalysts, such as, Bronsted and Lewis acids which are very noxious and corrosive. Mag-H$^+$ is a montmorillonite sheet silicate clay exchanged with protons. The structure of the obtained macromonomers was confirmed by Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance (NMR) and UV-visible spectroscopy. The presence of the methacrylate end groups of bis-macromonomers was determined by UV-visible spectroscopy. In order to find the optimal reaction conditions, effects of reaction time and the amount of anhydrides (AA and MA) on the yield of macromonomers were investigated.

Keywords: functionalized polymer, 3-glycidoxypropyl-trimetoxysilane, montmorillonite, eco-catalyst, cationic polymerization.

1. Introduction

Macromonomers or bis-macromonomers are linear macromolecules, with low molar mass, carrying polymerizable function at one or two chain ends. Bis-macromonomers have occupied a primordial place in the chemistry of macromonomers.

Several macromonomers and bis-macromonomers have been prepared by different polymerization and copolymerization process.[1-7] The main interest of the bis-macromonomers lies in their use in the synthesis of degradable amphiphilic or hydrophilic polymeric or copolymeric networks.[8-14]

Nevertheless, the initiators and catalysts used for these syntheses are expensive and often toxic, which requires several steps for the synthesis and the purification of the final product.

While respecting the environment, 3-glycidoxypropyltrimethoxysilane (GPTMS) is one of the coupling agents most used in the field of surface conversion treatment.[16-18] Several syntheses of hybrid organic-inorganic compounds were used: *via* sol-gel method, by the ring opening of epoxy ring of GPTMS, using an acid[19-26] or a base[27,28] as a catalyst. These hybrid inorganic-organic materials have several important applications in many different fields,[29-37] because they are distinguished by their enhanced mechanical strength and thermal stability.[26,38]

The main purpose of this work is to use a simple and safe processing method without using high temperature to prepare a functional linear PGPTMS macromonomers, in the presence of an anhydride. The polymerization reaction is realized under mild conditions, using an Algerian proton exchanged montmorillonite clay called Maghnite-H$^+$ (Mag-H$^+$), a natural and nontoxic cationic initiator, in a way to be in the context of green chemistry.

By acid activation of raw Maghnite with a 0.25M H$_2$SO$_4$ solution, there is a complete cationic exchange of Maghnite by protons, without destroying its structure.[39] The Mag-H$^+$ obtained is widely used in the ring-opening polymerizations[26,40-45], also in the synthesis of bis-macromonomers[6,7,46], and it has many advantages such as very low purchase price compared to other catalysts and the easy removal of the reaction mixture, regenerated by heating to a temperature above 373 K.[40,41] In our work, we were interested in using a new method for a green synthesis of telechelic PGPTMS with acetate and methacrylate end groups, in bulk, using one step, by cationic ring-opening polymerization of 3-glycidoxypropyltrimethoxysilane (GPTMS), in the presence of acetic anhydride (AA) and methacrylic anhydride (MA), using a green catalyst Mag-H$^+$ without spending energy. The best

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results in term of activation and yield of the product are determined using the kinetic study on the evolution of the synthesis reaction. FT-IR, ^{1}H NMR, and UV-Visible analysis show that the PGPTMS macromonomers were successfully obtained. The effects of different synthesis parameters, such as the amount of AA and MA, and reaction time, were discussed.

2. Experimental

2.1. Materials

Raw Maghnite (Algerian, natural montmorillonite clay) was obtained from BENTAL (Algerian Society of Bentonites) and used as catalyst. 3-Glycidyloxypropyl-trimethoxysilane (GPTMS, 98 %) was used as monomer for synthesis of PGPTMS, dichloromethane (CH_2Cl_2, 99.9 %) was used for polymer extraction and methanol (99 %) was used for precipitation. Acetic anhydride (98 %) and methacrylic anhydride (98%) were used for the preparation of functionalized PGPTMS. All these materials were used as received from Sigma-Aldrich, without further purifications.

2.2. Structural Analysis

The following methods were used:

Fourier Transformed Infrared Spectroscopy analysis (FT-IR) using a Perkin Elmer Two FT-IR instrument with an ATR sampling accessory.

X-Ray Diffraction (XRD) was conducted at room temperature with a Bruker AXS D8 advanced X-ray diffractometer (40 kV, 30 mA) using Cu-Kα radiation ($\lambda = 0.154$ nm) at the rate of 2 min^{-1} in the 2θ range of 2.0–80°.

^{1}H NMR (Nuclear Magnetic Resonance) measurements were carried, using an Avance Bruker NMR Spectrometer at 300 MHz. $CDCl_3$ was applied as solvent. Chemical shift reference was tetramethylsilane (TMS).

Differential Scanning Calorimetry (DSC) studies were carried out with a Netzsch DSC 204 F1 Phonix 240-12-010-L instrument. Samples were heated at site average scan of173–373 K with a heating rate of 10 K/min.

The UV-VIS analyses were performed with a SPECORD 210 Analytik Jena spectrometer at room temperature, in the wave range of 200–450 nm.

2.3. Procedures of Synthesis

2.3.1. Preparation of the Mag-H$^+$ catalyst

Mag-H$^+$ was prepared by activation of the raw Maghnite with sulfuric acid solution (0.25 M), using a method similar to that described in our previous-study.[26,40,41] Crushed raw Maghnite (30 g) was dispersed in distilled water (1 L). The mixture was stirred well at room temperature, then left to settle for about 8 h in a volumetric test tube until the appearance of montmoril-lonite supernatant. After that about 100 mL of supernatant was taken and replaced by 100 mL of distilled water, the mixture was stirred again and left to settle for another 8 h. This operation was repeated until the maximum of montmorillonite was recovered. Then, a solution of sulfuric acid H_2SO_4 (0.25 M) was added to the recovered dried montmorillonite. The solution thus obtained was stirred for two days, to exchange the cation ions present in the clay by H$^+$ ions. Then the formed catalyst (Mag-H$^+$) was filtered after being washed several times with distilled water up to pH 7. The Mag-H$^+$ was dried in an oven for 24 h at 378 K and then crushed. The catalyst was characterized by FT-IR and XRD analyses.

2.3.2. Polymerization of GPTMS

The ring-opening polymerization of 3-glycidoxypropyltrimethoxysilane (GPTMS) was carried out in bulk – a mixture of 2 mL of GPTMS (0.0084 mol) and dried Mag-H$^+$ (20 wt. %) were stirred for 8 h at room temperature (293 K). At the end of the reaction, the mixture was filtered to remove the catalyst and precipitated in 50 mL of cold methanol (CH_3OH). The resulting polymer was extracted by filtration, washed for several times and dried in vacuum overnight and weighed. The polymerization reaction of GPTMS is described in Scheme 1.
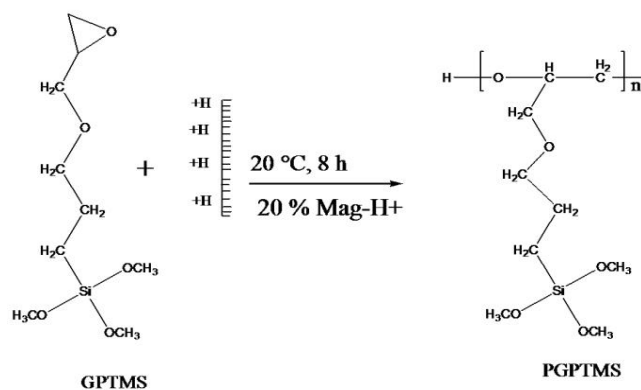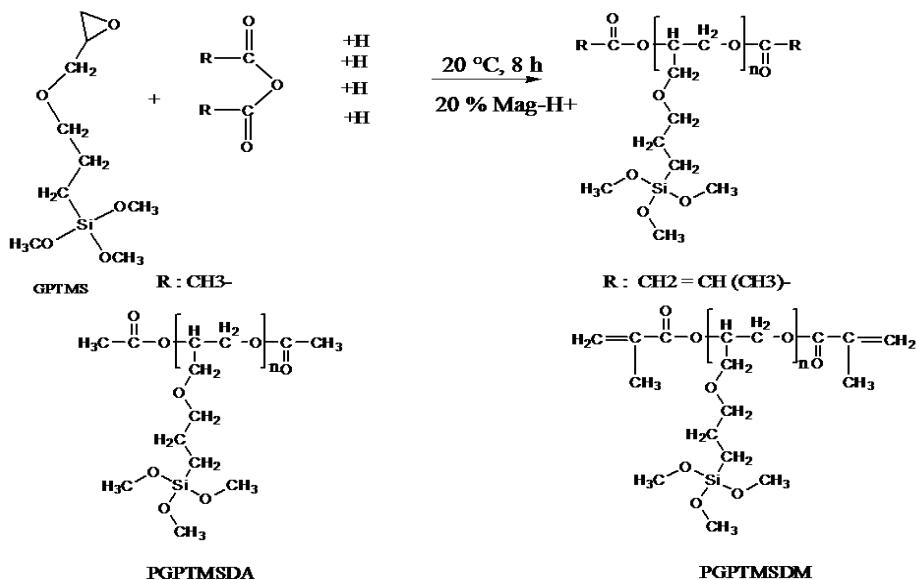

Scheme 1. Polymerization reaction of GPTMS in bulk

2.3.3. Synthesis of PGPTMS di-acetate (PGPTMSDA) and PGPTMS di-methacrylate (PGPTMSDM)

Macromonomers of GPTMS were obtained by ring-opening polymerization of GPTMS in the presence of anhydrides, catalyzed by Mag-H$^+$, in a single step, in bulk (Scheme 2). Each acetate and methacrylate group is linked to the polymer chain-end by an ester function.

In two volumetric flasks containing 2 mL of GPTMS (0.0084 mol) and 20 wt. % of dried Mag-H$^+$, we added 3 wt. % of acetic anhydride (AA) and methacrylic anhydride (MA), respectively. Each mixture was stirred for 8 h at room temperature (293 K). After the reaction time, the catalyst was removed by simple filtration after adding 1 mL of dichloromethane (CH$_2$Cl$_2$). The filtrate was purified by extraction (methanol/water). PGPTMSDA and PGPTMSDM were extracted by filtration, washed for several times and dried under vacuum overnight. The same procedure was repeated by changing the amount of anhydride and time reaction of the synthesis of PGPTMSDA and PGTMSDM macromonomers in order to find the optimal reaction conditions.

The operating conditions and the yields of the three synthesizes, are presented in Table.

Scheme2. Synthesis reaction of PGPTMSDA and PGPTMSDM macromonomers in bulk

Table. Summary of the operating conditions for the polymerization of GPTMS with and without anhydride

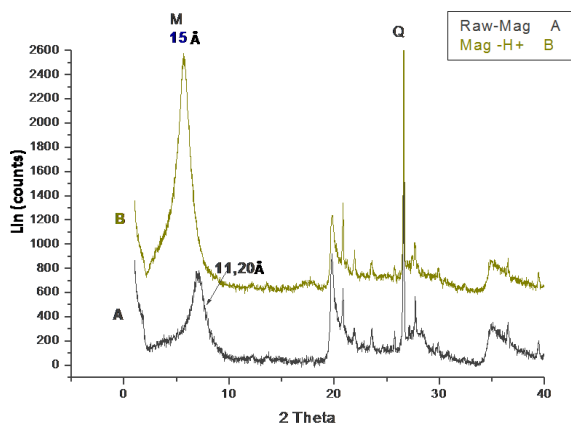| Samples	GPTMS, mol	Mag-H$^+$, %	AA, %	MA, %	Time, h	Yield, %
PGPTMS	0.0082	20	–	–	8	25
PGPTMS di-acetate	0.0082	20	3	–	8	35
PGPTMS di-methacrylate	0.0082	20	–	3	8	28

Fig. 1. X-Ray diffractograms of raw-Mag (A) and Mag-H$^+$ (0.25M) (B). M is Montmorillonite, Qis quartz
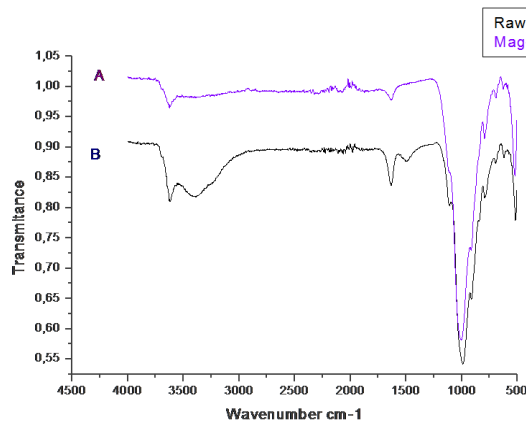

Fig. 2. FT-IR spectra of raw-Mag (A) and Mag-H$^+$(0.25M) (B)

3. Results and Discussion

3.1. Characterization of Mag-H$^+$(0.25M)

In order to check the quality of the Mag-H$^+$ preparation, the sample analysis by X-ray diffraction (XRD) and FT-IR were carried out.

X-ray diffractograms of the raw Maghnite and Mag-H$^+$ are shown in Fig. 1. An increase in basal spacing from 11.20 Å for raw Maghnite – characteristic of a single water layer between sheets, to 15 Å – the distance attributed to two interlamellar water layer in Mag-H$^+$, reflecting the cationic exchange of the cation ions (Na$^+$, Ca^{2+}, K$^+$, NH$_4^+$, Mg^{2+}) and a substitution of the H$^+$ ions in montmorillonite, being associated with hydration state resulted from the acidtreatment.[14,43,44]

FT-IR spectrum of Mag-H$^+$ (0.25M) and raw Maghnite are shown in Fig. 2.The vibrations of hydroxyl groups around 3400 and 3600 cm^{-1} correspond to the hydrated structure of Mag-H$^+$. Other absorption bands at 1004 (Si–O), 780, 520 and 500 cm^{-1}can be attributed to the montmorillonite clay structure, which is in a good agreement with literature data.[47-49]

3.2. Characterization of PGPTMS, PGPTMSDA and PGPTMSDM

3.2.1.FT-IR analysis

FT-IR spectrum of monomer (GPTMS) and macromonomers PGPTMS synthesized in bulk, PGPTMSDA and PGPTMSDM are shown respectively in Figs. 3a, b, c, and d. The characteristic absorption peaks of epoxy groups[49,50] observed at around778–815 and 900–910 cm^{-1}

in the spectrum of the monomer (Fig. 3a) disappeared completely in the spectrum of the obtained macromonomers: PGPTMS (Fig. 3b), PGPTMSDA (Fig. 3c) and PGPTMSDM (Fig. 3d). The spectrum of GPTMS was compared with those of PGPTMS, PGPTMSDA and PGPTMSDM macromonomers. The characteristic absorption band of the epoxy group, which can be seen at around 910 cm^{-1} in the spectrum of the monomer, disappeared completely after polymerization of GPTMS with or without anhydride, in the presence of acidic catalyst. This indicates the great possibility of ring-opening polymerization of GPTMS monomer. Characteristic bands of GPTMS epoxy ring in the FT-IR spectrum of PGPTMS were assigned based on literature data.[19-23,51] These bands were located at 500 cm^{-1} (Si–O in Si–O–CH$_3$); 734 and 841 cm^{-1} (C–C), 1089 cm^{-1} (–CO in Si–O–CH$_3$); 1190 cm^{-1} (–CO in C–O–C); 1016 cm^{-1} (–CO epoxy ring); 1480 cm^{-1}(–CH); 2800–3000 cm^{-1} (–CH$_2$ and –CH$_3$) and 3360 cm^{-1} (–OH). In addition to the bands observed in Fig. 3b (PGPTMS), the FT-IR spectrum of macromonomer PGPTMSDA (Fig. 3c) shows a band around 1740 cm^{-1} that corresponds to the valence vibration of the C=O of ester group and another band at 3387 cm^{-1} that corresponds to the hydroxyl end group. The presence of the unsaturated end group of macromonomer PGPTMSDM was determined by FT-IR analysis as shown in Fig. 3d, the bands characteristic of C=O are present between 1720 and 1790 cm^{-1}. Methacrylate group is linked to the polymer chain-end by an ester function. A less intense band at 1640 cm^{-1} corresponds to the valence vibration of the C=C bond. The results obtained by FT-IR analysis confirm the successful synthesis of GPTMS macromonomers using Mag-H$^+$ without or with anhydrides.
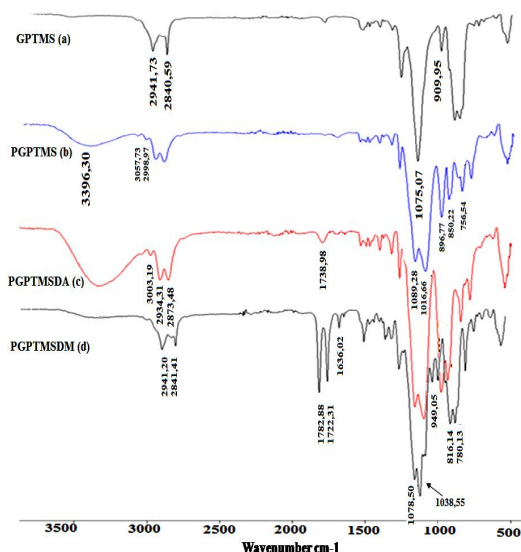

Fig. 3. FT-IR spectra of GPTMS (a), PGPTMS (b), PGPTMSDA (c), and PGPTMSDM (d) macromonomers
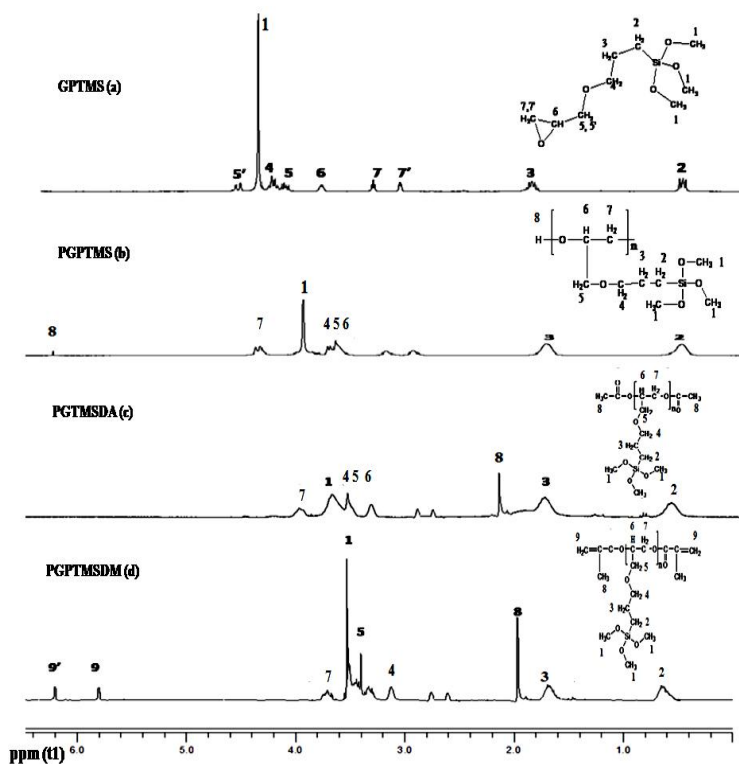
Fig. 4. ^{1}H NMR spectra of GPTPMS (a), PGPTMS (b), PGPTMSDA (c),
and PGPTMSDM(d), prepared at 293 K for 8 h

3.2.2. ^{1}H NMR analysis

The chemical proton displacements for GPTMS and macromonomers PGPTMS, PGPTMSDA and PGPTMSDM are shown in Fig. 4.

Comparing two spectra of GPTMS monomer and PGPTMS polymer prepared in bulk (Scheme 1), the change in chemical shift and coupling of the resonances of H6, H7 and H7' in the spectrum of the polymer can be observed. The appearance of multiplets around 3.2 and 3.4 ppm corresponding to protons H4, H5 and H6 of PGPTMS after ring-opening polymerization can be seen, which is in a good agreement with literature data.[20,22,51] The signal at 3.48 ppm corresponding to the protons in alkoxide group (Si–O–CH$_3$) in two spectra confirms that only the ring opening polymerization is set up keeping the alkoxide function, whereas the appearance of a peak at 5.4 ppm indicates the hydroxy end group O–H of polymer product resulting from the opening of epoxide rings. The proton chemical shifts of the synthesized polymer are in agreement with the literature data.[19-23, 51]

The ^{1}H NMR measurements (Fig. 4c) confirm the structure of macromonomer PGTMSDA resulted from the polymerization reaction of GPTMS with acetic anhydride (Scheme 2). Apart from the proton signals, the appearance of signal originating from methyl ester end group around 2.15 ppm (Fig. 4b) can be noted, which is characteristic for the polymer chain.

3.2.3. DSC analysis

Thermal properties of the obtained PGPTMS and PGPTMSDA macromonomers were determined by Differential Scanning Calorimetry (DSC) and are shown in Fig. 5. The glass-transition temperature (*Tg*) of PGPTMS is below 243 K (241.73 K). This result is in accordance with previous literature data.[51] The low *Tg* indicates the good resistance of the polymer at low temperature. On the other hand, the glass transition temperature of PGPTMSDA prepared by end capping with acetic anhydride is observed at 334 K. These results show the formation of new structure of macromonomer with Mag-H^{+}.

3.2.4. UV-Vis analysis

The presence of the unsaturated end groups was also determined by UV analysis. The curve shown in Fig. 6 represents the UV-Vis spectrum of PGPTMSDM prepared in bulk by end capping with methacrylic anhydride. PGTMSDM was diluted in dichloromethane (2 mg/mL) and then its absorbance was measured. The spectrum shows the maximum absorbance at about $\lambda = 245$ nm, indicating the presence of the double bond;[6,7] this is in a good agreement with the results of FT-IR and the ^{1}H NMR analysis.
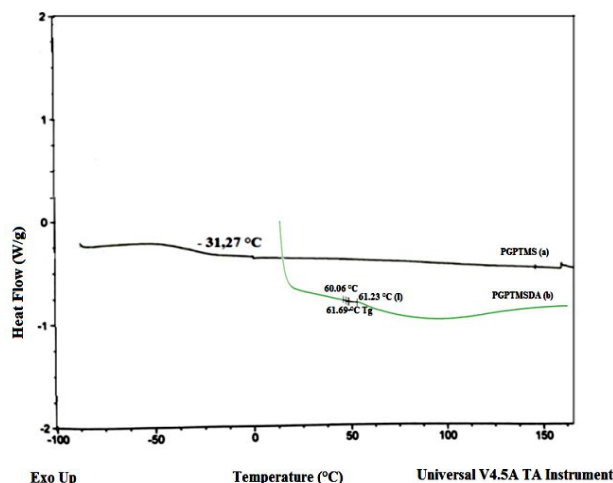
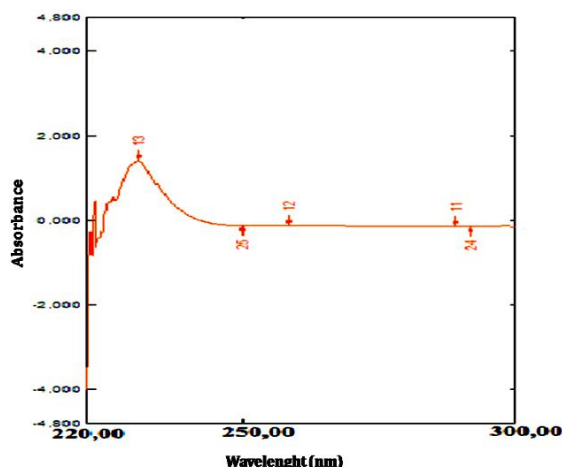**Fig. 5.** DSC curve of PGPTMS (a)
and PGPTMSDA (b)

Fig. 6. UV-Vis spectrum
of PGPTMSDM in CH_2Cl_2

3.3. Kinetic Study of the PGPTMSDA and PGPTMSDM Synthesis

The objective of this part is to study the effect of various parameters, including the amount of the catalyst on the synthesis of PGPTMS, as well as the amount of anhydride and time reaction on the synthesis of PGPTMSDA and PGTMSDM. The reactions conditions were optimized from the standpoint of the obtained macromonomers yield. Some results are shown in Figs. 7-9.

3.3.1. Effect of Mag-H$^+$ amount on the PGPTMS yield[26]

In our previous work[26], various amounts of Mag-H$^+$ (5; 10; 15; 20 and 25 wt.%) were used for the synthesis of PGPTMS by the ring-opening of the epoxide at 293 K for 8 h. As shown in Fig. 7[26], the yield increases with the amount of catalyst, however, the use of higher amount of Mag-H$^+$ causes a certain lowering of the polymer yield. The highest yield of polymerization was observed with 20 wt.% of Mag-H$^+$. Similar results were obtained by Belbachir and coworkers.[6,41-43] For studying the effect of the anhydride amount and synthesis time of PGPTMSDA and PGTMSDM on the yield of the obtained macromonomers, 20 wt.% of Mag-H$^+$ was used.[26]

3.3.2. Effect of anhydride amount on the PGPTMSDA and PGPTMSDM yield

The synthesis of PGPTMS macromonomers with acetate end groups (PGPTMDA) or with methacrylate end groups (PGPTMSDM) was carried out at 293 K with 20 wt.% of Mag-H$^+$ for 8 h in bulk, using various amo-

unts of acetic anhydride (AA) and methacrylic anhydride (MA) (1; 2; 3; 5; and 10 wt.%). Fig. 8 shows that the yield of PGPTMSDA and PGPTMSDM macromonomers increases with the amount of AA and MA and reaches its maximum of 35 % (PGPTMSDA) and 28 % (PGPTMSDM) at 3 wt.% of AA and MA, respectively. These results are due to multiplication of active centers. However, the yield decreases with increasing of acetic and methacrylic anhydride proportion. This result is likely to originate from increasing of acetic acid or methacrylic acid molecules formed during the activation of acetic and methacrylic anhydride with Mag-H$^+$, responsible of alteration of polymer chain growing (termination step). This result is in accordance with previous studies.[6,7, 42-44]

3.3.3. Effect of the reaction time on the PGPTMSDA and PGPTMSDM yield

The effect of reaction time on the PGPTMS macromonomers yield was studied at 293 K with 20 wt.% of Mag-H$^+$, using 3 wt.% of anhydride (AA, MA) in bulk at various reaction times: 2, 3, 5, 8 and 24 h. The results are shown in Fig. 9. The yields of PGPTMSDA and PGPTMSDM macromonomers increase with reaction time. The yield of PGPTMSDA macromonomer reaches a maximum of 60 % after 24 h of reaction, whereas the yield of PGPTMSDM macromonomer reaches a maximum of 28 % after 8 h of stirring. After this time both yields decrease. This result can be interpreted by the saturation of the active sites of methacrylic anhydride or the presence of chain transfer reactions which are common for polymerization with a cationic catalyst.
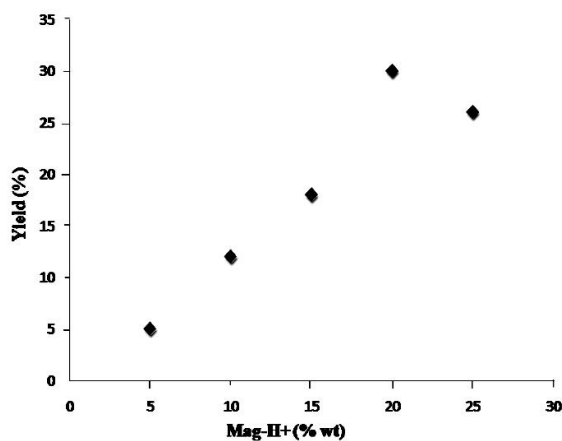
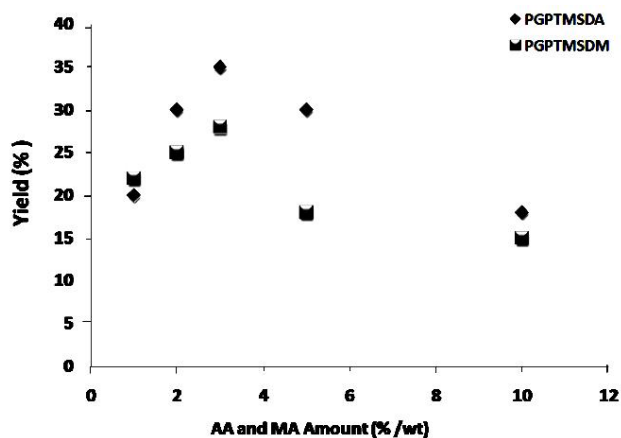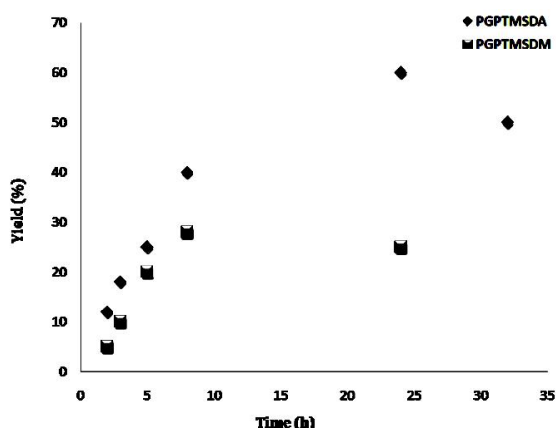**Fig. 7.** The effect of Mag-H$^+$ amount on the PGPTMS yield: in bulk at 293 ± 2 K for 8 h[26]

Fig. 8. The effect of AA and MA amount on the PGPTMS diacetate (PGTMSDA) and PGTMS dimethacrylate (PGTMSDM) yield; in bulk at 293 ± 2 K


Fig. 9. The effect of time on the PGPTMS diacetate (PGTMSDA) and PGTMS dimethacrylate (PGTMSDM) yield; in bulk at 293 ± 2 K

3.4. Mechanism of Polymerization

The proposed mechanism of the cationic ring-opening polymerization of GPTMS in the presence of an anhydride is schematized as following:
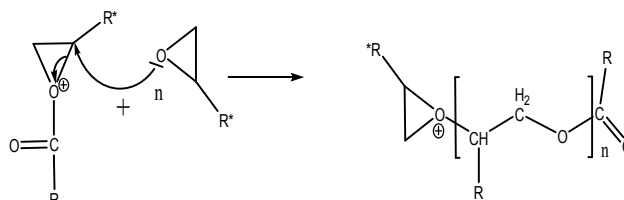
1. Initiation.

The protonation of anhydride (methacrylic or acetic anhydride) by Mag-H$^+$. Then, initiation occurs through formation of a secondary oxonium ion derived from the monomer.
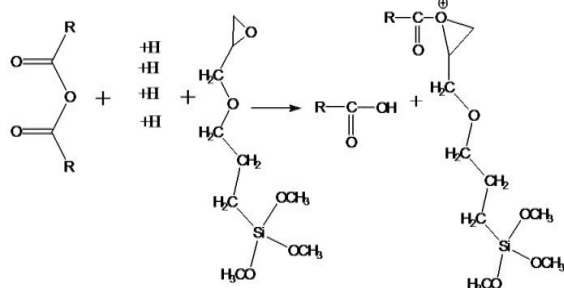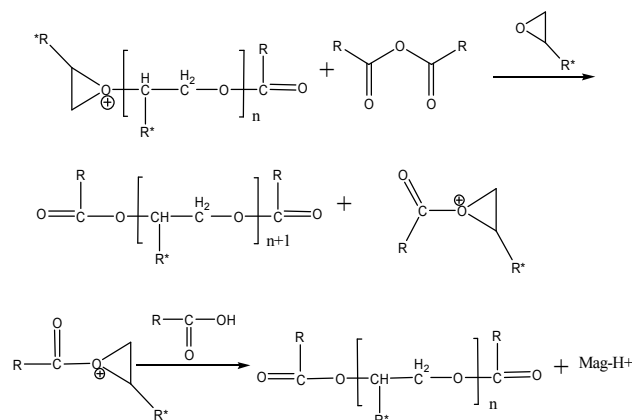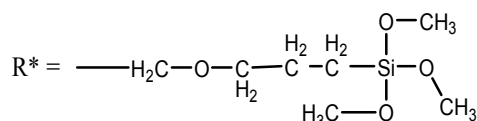

2. Propagation.

The propagation takes place through nucleophilic attack of oxygen onto a carbon of the oxonium ion.

3. Termination and chain transfer.

where R are CH$_3$–; CH$_2$=CH (CH$_3$)–

R* = ———H_2C—O—C—$\underset{H_2}{C}$—$\overset{H_2}{C}$—$\underset{H_3C—O}{\overset{O—CH_3}{Si}}$—O—$CH_3$

4. Conclusions

An acidic Maghnite-H$^+$ catalyst has been obtained by proton acid-exchanged process with H_2SO_4 and characterized by FT-IR and XRD analysis.

PGPTMS macromonomers were synthesized successfully under mild conditions, neither requiring very low or very high temperature nor high pressure, using a green catalyst in bulk, by the ring-opening polymerization of GPTMS in the presence of anhydride (AA, MA). The yield of the macromonomers obtained depends on the amount of Mag-H$^+$ and anhydride used and the reaction time. The optimum reaction conditions for the synthesis of PGPTMS macromonomers were defined as: 20 wt. % of Mag-H$^+$, 3 wt. % of anhydride (AA, MA), the reaction time of 8 h and temperature of 293 K. The structure of the obtained macromonomers has been confirmed by FT-IR, ^{1}H NMR and DSC analyses.

Further work involving PGPTMS macromonomers with methacrylic end groups for the synthesis of degradable hydrogels directly in water, is on the way.

Another interesting aspect concerns the fact that Mag-H$^+$ can be easily separated from the polymeric products and regenerated by heating to a temperature above 373 K.

Acknowledgments

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ЗЕЛЕНИЙ СИНТЕЗ ФУНКЦІОНАЛІЗОВАНОГО ПОЛІ(3-ГЛІЦИДОКСИПРОПІЛ-ТРИМЕТОКСИСИЛАНУ) З ВИКОРИСТАННЯМ ЕКОКАТАЛІЗАТОРА (ОБРОБЛЕНИЙ МОНТМОРИЛОНІТ)

Анотація. *Катіонною полімеризацією з відкриттям кільця 3-гліцидоксипропілтриметоксисілану і використанням ангідридів (оцтового ангідриду (АА) та метакрилового ангідриду (МА)), за відсутності розчинників, синтезований телехельний полі(3-гліцидоксипропілтриметоксисилан) з кінцевими ацетатними та метакрилатними групами. Замість електрофільних каталізаторів, таких як кислоти Бронстеда та Льюїса, дуже шкідливих та корозійних, як каталізатор процесу використано екологічний твердий Magnite-H⁺ (Mag-H⁺), який є йонообмінною силікатною глиною з монтморилоніту. Структуру отриманих макромономерів підтверджено методами інфрачервоної спектроскопії Фур'є, ядерно-магнітного резонансу та УФ-спектроскопії. Наявність кінцевих груп біс-макромономерів метакрилату визначено за допомогою УФ-спектроскопії. Встановлено оптимальні умови реакції, досліджено вплив часу реакції та кількості ангідридів (АА та МА) на вихід макромономерів.*

Ключові слова: функціональний полімер, 3-гліцидоксипропілтриметоксисилан, монтморилоніт, екокаталізатор, катіонна полімеризація.