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SUSTAINABLE POLYMERIZATION OF 1,3-DIOXOLANE FUNCTIONALIZED WITH BENZOIC ANHYDRIDE: A GREEN APPROACH WITH MAGHNITE-H$^+$

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Abstract. This study presents a green approach to the cationic polymerization of 1,3-dioxolane using Maghnite-H$^+$, a protonated Algerian montmorillonite clay, as an eco-friendly, non-toxic, and cost-effective catalyst. In combination with benzoic anhydride as a co-monomer, Maghnite-H$^+$ effectively initiated bulk polymerization without conventional toxic initiators. Reaction conditions were optimized by varying temperature, time, catalyst loading, and co-initiator concentration. The highest yield (52 %) was obtained at 25 °C after 1 hour. The resulting poly(1,3-dioxolane) was characterized by FT-IR, ^{1}H NMR, and UV-Vis spectroscopy, confirming successful polymer formation. Thermogravimetric analysis (TGA) indicated good thermal stability with a degradation temperature around 300 °C. Molecular weight, estimated by UV-Vis and ^{1}H NMR, was approximately 9700 g/mol, suggesting controlled polymerization. These findings demonstrate the potential of Mag-H$^+$ as a sustainable alternative catalyst, supporting environmentally friendly strategies in polymer synthesis and contributing to the development of green materials.

Keywords: 1,3-dioxolane, benzoic anhydride, green polymerization, maghnite-H$^+$, characterization.

1. Introduction

The polymerization by opening of cyclic monomers was studied by several researchers due to its interesting properties.[1–5] The cyclic alkanes do not possess in their structure the connections susceptible to being easily attacked by a catalyst; the presence of a heteroatom creates a nucleophilic or electrophilic catalyst to attack this privileged site and to activate a polymerization by opening of the cycle. 1,3-dioxolane or ethylene glycol formalin, a heterocyclic monomer belonging to the acetal family, is characterized by the big oxygen atom nucleophile of the polymer chain. The polymerization of 1,3-dioxolane has been carefully investigated by Penzeck *et al.*[6]

Poly(1,3-DXL)-based macro monomers of a highly hydrophilic character have been widely studied due to their multiple applications, their repetitive unit contains the acetals and the oxythylene groups.[7–11] The hydrogels of poly (1,3 DXL) were obtained for the first time by multiple coupling of the extremities hydroxyls of the poly (1,3 DXL) chains, with the opposing functions of a multifunctional iso-cyanate.[12] However, the presence of these products as well as iso-cyanate in the gel, cannot be used for biomedical applications.

Recently, poly(1,3-DXL) gels were prepared by radical homo-polymerization of bis-macromonomers such as methylmethacrylate, styrene, butylmethacrylate and also by hydrophilic monomers such as hydroxy-2-ethylene methacrylate (HEMA) in aqueous and organic environments.[13, 14] Several catalysts were tested to obtain good yields of bis-macromonomers of poly(1,3-DXL), but also to develop a simple and effective method for this type of polymer.[15, 16] However, these catalysts present a major problem due to their toxicities and higher cost. To date, several attempts have been proposed to prepare efficient non-toxic and recyclable catalysts for the preparation of poly(1,3-DXL).[17]

The main purpose of this work is to investigate the catalytic properties of a natural clay (Mag-H+) as a new and non-toxic catalyst for one-pot synthesis of poly(1,3-DXL) with benzoic anhydride. In our previously published work, we have shown the advantages of different applications of this catalyst type in several polymerization reactions.[18, 19] It is preferred for its many advantages, such as a very low purchase price compared to other catalysts and the easy removal of the reaction mixture, regenerated by heating to a temperature above 100°C.[20–22] In this work, a very detailed study on the catalytic properties of Algerian clay (Mag-H+) is developed and discussed in terms of efficiency. FT-IR, ^{1}H NMR, UV-Vis, and TGA analysis indicate that the functionalized polymer poly(1,3-DXL) with benzoic anhydride has been successfully obtained.

2. Experimental

2.1. Materials

1,3-dioxolane, benzoic anhydride, methanol (CH_3OH, 98 %), sulfuric acid (H_2SO_4, 99.9 %), and dichloromethane (CH_2Cl_2, 99.8 %) were supplied by Sigma Aldrich and used as received. The Maghnite, Algerian montmorillonite silicate sheet clay was supplied in the raw state by ENOF Bental Spa of the National Company of Nonferrous Mining Products, Maghnia Unit (Algeria), and all other regents were used without further purification.

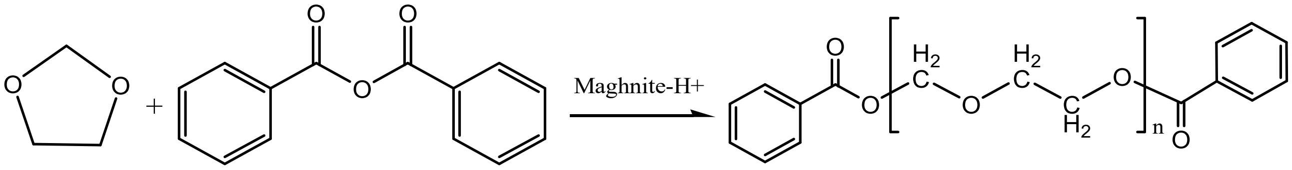
2.2. Methods

2.2.1. Activation of Maghnite-H$^+$ (Mag-H$^+$)

Mag-H$^+$ is prepared according to the process reported in our previous study.[23] In an Erlenmeyer flask of 1000 ml, a mixture of 30 g of raw-Maghnite (Raw-Mag) and 500 ml of distilled water was prepared and stirred for 2 hours, then sulfuric acid (0.25 M) was added and stirred for 48 hours at room temperature with a magnetic stirrer. The obtained mixture was filtered, washed several times with distilled water, and then dried at 105 °C for 24 hours. The solid was crushed to obtain the form of a fine powder, and finally stored away from the air and moisture. Before each use, the Mag-H$^+$ was dried at a temperature of 105 °C for 30 min to eliminate the adsorbed water.

2.2.2. Polymerization procedure

In a flask, the monomer (1,3-DXL) with benzoic anhydride was mixed, then a catalyst amount (3 wt. % of Mag-H$^+$) was added. The reaction mixture was stirred at 25 °C for 1 hour. The extraction of the catalyst was made by filtration after the addition of 10 ml of dichloromethane (CH_2Cl_2). The filtered solution was evaporated, and then thoroughly purified by precipitation in cold methanol (CH_3OH). This purification step was repeated to effectively remove all unreacted monomers and residual products. The obtained polymer was isolated by filtration and dried in a vacuum overnight.



Scheme 1. Polymerization of 1,3-dioxolane with benzoic anhydride

2.3.3. Characterization methods

X-ray diffraction analysis (XRD) was carried out at room temperature on a Brucker D8 Advance X-Ray diffractometer (40 kV, 30 mA) using CuKa radiation (*k* = 0.154 nm) at the rate of 2°/min in the 2θ range of 2.0–80°. The morphology of the Maghnite was studied using a field emission scanning electron microscopy (FEG-SEM) on a Thermo Fisher (Apreo 2C) electron microscope. NMR is a very powerful analytical method for the elucidation of chemical structures. ^{1}H NMR spectra were recorded on a Brucker-Avance 400 MHZ apparatus in deuterated chloroform, $CDCl_3$. Fourier Transform Infrared Spectroscopy (FT-IR) was performed by a Brucker Alpha spectrometer equipped with an ATR Diamond. UV-Vis diffuse reflectance spectra were recorded using a SPECORD 210 Analytik Jena spectrometer. Thermal properties were analyzed by thermogravimetric analysis (TGA) using PerkinElmer STA 6000 under air and nitrogen in the temperature range of 30–700 °C with a heating rate of 20 °C/min.

3. Results and Discussion

3.1. Characterization of Mag-H$^+$

The infrared spectra of raw-Mag and Mag-H$^+$ are shown in Fig. 1. The broad band at 3500 cm^{-1} corresponds to OH groups linked to octahedral aluminum. The intense band at 1004 cm^{-1} is assigned to the valence vibration of Si-O in the tetrahedral layer. A weak band is observed at 780 cm^{-1} that is attributed to the tetravalent silicon due to the presence of amorphous silica. The comparison of this band intensity in the spectra of both materials allow deducing that there is an alteration of the structure, reflected by the increase of this intensity during acid treatment.[24]

The XRD patterns of Raw and the modified clay are represented in Fig. 2. The interlayer distances of both materials are obtained by Bragg's equation. The calculated interlayer distance of Mag-H$^+$ is 1.454 nm. This is probably due to the size of H_3O^+ ions, leading to an increase in the interlayer distance. The peak (d_{001}) of Mag-H$^+$ is more intense than that of Raw-Mag, due to the location of the H_3O^+ ions in the interlayer distance of Maghnite.[25]

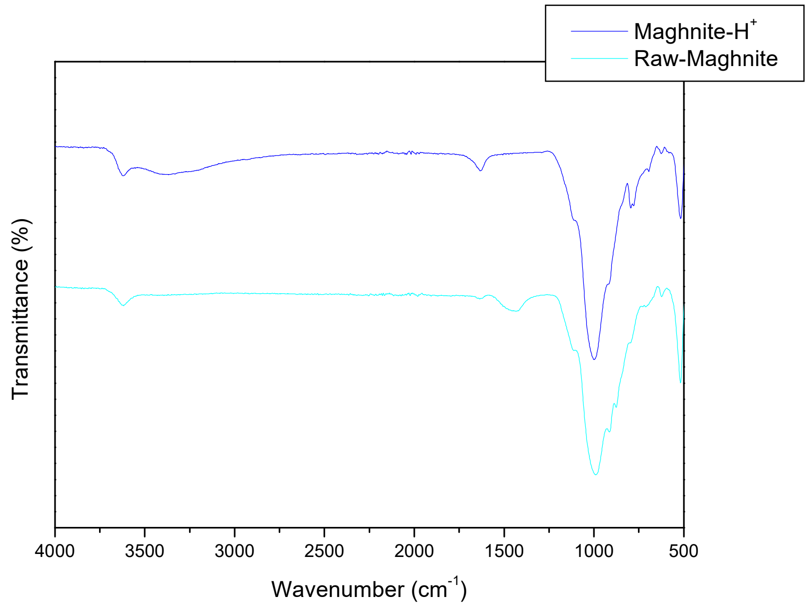


Fig. 1. FT-IR spectrum of Mag-H$^+$ and Raw-Mag

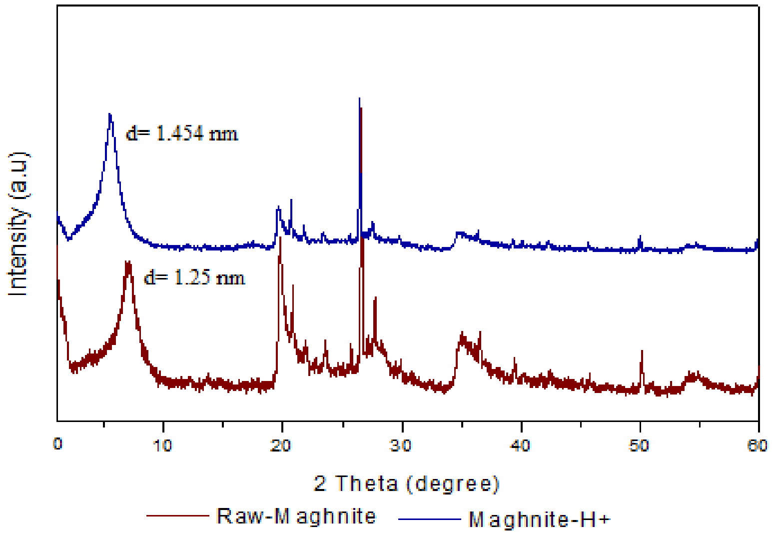


Fig. 2. XRD patterns of Mag-H$^+$ and Raw-Mag

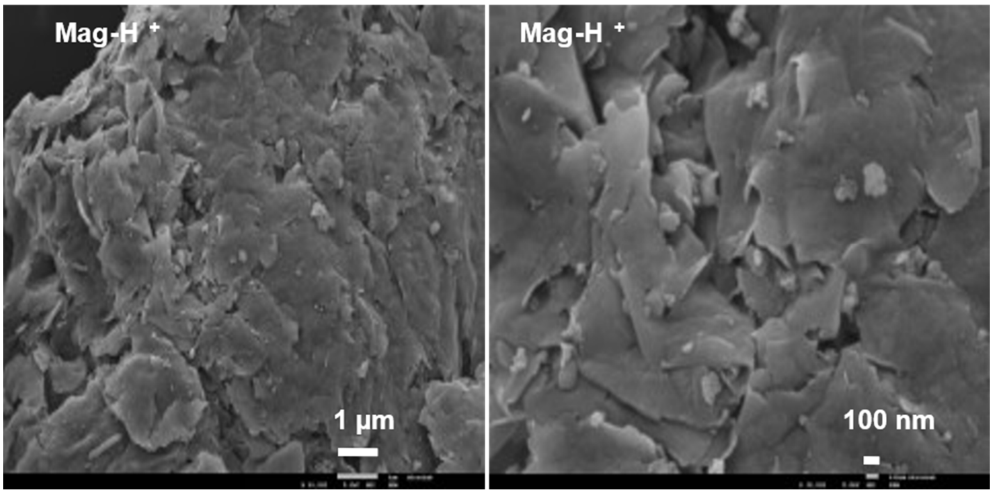


Fig. 3. SEM images of Mag-H$^+$ at 1 µm and 100 nm

The scanning electron microscopy (SEM) images (Fig. 3) show the surface morphology of Mag-H$^+$ at two different magnifications. The image on the left, taken at lower magnification (1 µm scale), reveals a compact and aggregated structure composed of irregularly shaped, plate-like particles, indicative of strong interparticle interactions. In contrast, the higher magnification image on the right (100 nm scale) highlights a more exfoliated and layered morphology, with visible thin, stacked platelets. This structure suggests improved dispersion and possible delamination of the clay layers, likely resulting from chemical modification during the activation process. The observed layered architecture increases the surface area and exposes more active sites, which is advantageous for its role as a solid acid catalyst. Such morphology facilitates monomer diffusion and enhances catalytic efficiency during polymerization.

3.2. Characterization of the obtained polymer

FT-IR spectroscopy was used to determine the different functional groups of the obtained polymer. As shown in Fig. 4, it is characterized by different vibration bands. The band at 1719.40 cm^{-1} corresponds to the carbonyl groups (C=O) of ester.

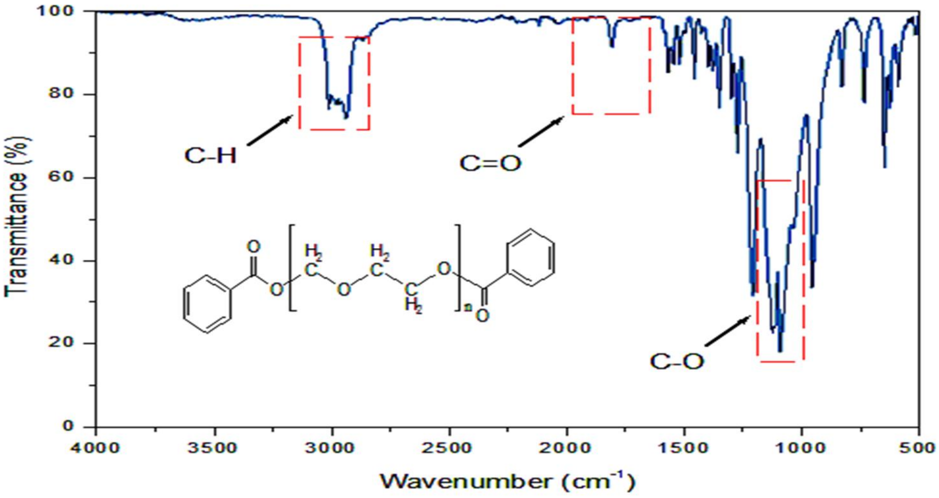


Fig. 4. FT-IR spectrum of the obtained polymer

The bands between 2881–2956 cm^{-1} correspond to the vibrations of C–H of the methyl group. The band at 1450 cm^{-1} is assigned to the vibrations of C–C. The bands at 1018 and 1300 cm^{-1} are attributed to C–O groups of ether and ester functions.[26] The bands at 1473 and 716 cm^{-1} correspond to the vibration of benzene groups.

^{1}H NMR spectrum of the obtained polymer is shown in Fig. 5. The ^{1}H NMR spectrum of the obtained polymer exhibits three distinct chemical shifts, confirming its expected structure. The signal observed at $\delta = 4.74$ ppm (a) corresponds to the methylene protons of the -O-CH$_2$-O- moiety, characteristic of the dioxolane ring. The peak at $\delta = 3.71$ ppm (b) is assigned to the protons of the -O-CH$_2$-CH$_2$-O- group, further supporting the successful polymerization of 1,3-dioxolane. Additionally, the signal at $\delta = 7.55$ ppm (c) is attributed to the aromatic protons of the benzoic anhydride unit, confirming its incorporation into the polymer structure. These NMR results, in conjunction with FT-IR and UV-Vis analyses, strongly support the successful synthesis of poly(1,3-DXL) using Mag-H$^+$ as a catalyst.

The thermogravimetric analysis (TGA) of the synthesized poly(1,3-DXL) provides valuable insight into its thermal stability. As shown in Fig. 6, the TGA curve exhibits a single, sharp weight loss step beginning around 300 °C and concluding near 400 °C, indicating a one-step thermal degradation process. The polymer remains thermally stable up to approximately 300 °C, suggesting good resistance to thermal decomposition under inert conditions. The absence of initial weight loss confirms the effective removal of residual solvents and volatile impurities. The rapid mass loss in the main degradation region is characteristic of depolymerization. Such degradation is attributed to the depolymerization mechanism, where the polymer chains break apart into their original monomers, as commonly seen in acetal-based polymers like poly(1,3-DXL). The negligible residual mass beyond 400 °C further indicates the absence of significant char formation, pointing to a clean degradation process. Overall, the TGA results confirm the successful synthesis of a structurally homogeneous polymer with moderate thermal stability, making it suitable for applications requiring thermal endurance up to 300 °C.

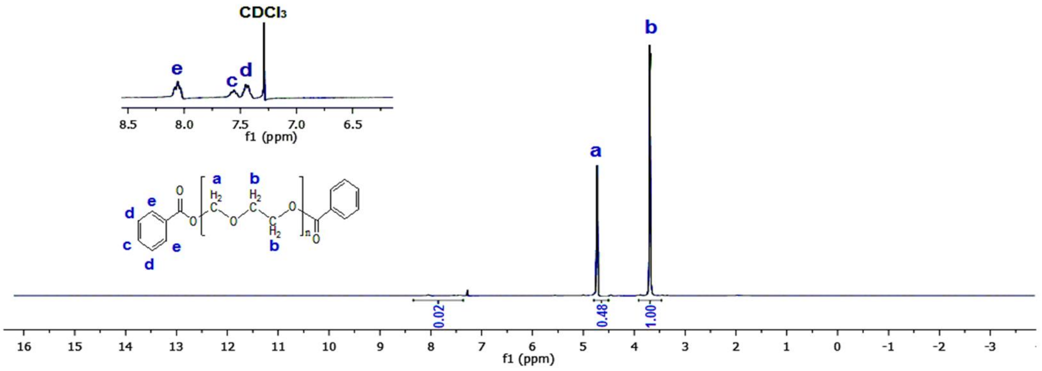


Fig. 5. ^{1}H NMR spectrum of the resulted polymer

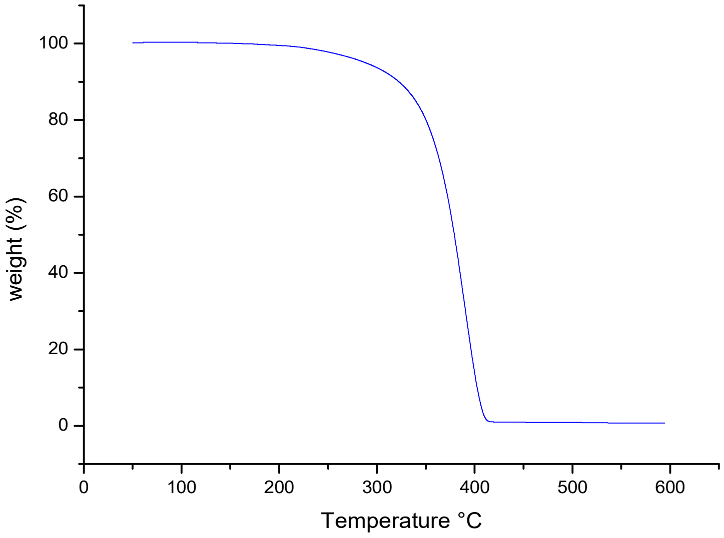


Fig. 6. Thermogravimetric (TGA) analysis of the resulted polymer

UV-Vis analysis allows assaying the terminal chromophore groups of the chain to access the average mass Mn. Methyl benzoate is taken as a model bearing the same type of chromophore as our polymers to determine the number-average molar mass with $\lambda = 230$ nm and $\varepsilon = 20000$ L.mo1^{-1}.cm^{-1}.

According to the Berr – Lambert law, $D_o = \varepsilon \times 1 \times c$ with $l = 1$ cm. The knowledge of ε and the optical density D_0 of the chromophore of the polymer chain allow the determination of its concentration C (mol/L) = D_0/ε^1.

CH_2Cl_2 was taken as a solvent, and 0.1 g of each sample was diluted in 50 ml of solvent, and then its absorbance was measured. For the second sample (effect of catalyst), UV was used to calculate the molar mass.

$Mn_{(uv)} = C_{theo}/C_{exp} = 2/2.066.10^{-4} = 9700$ g/mol.

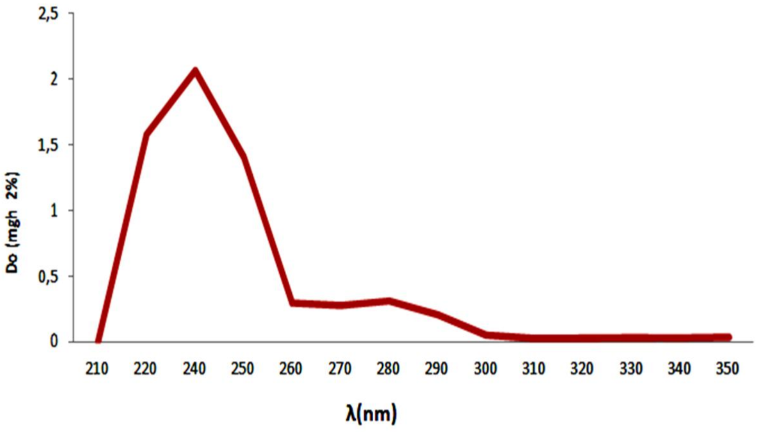


Fig. 7. UV spectrum of the resulted polymer

3.3. Kinetic studies

The objective of this part is to study the kinetic of the 1,3-dioxolane polymerization by Mag-H$^+$, which consists in varying separately different parameters including the quantity of the catalyst, the reaction time, the amount of Benzoic Anhydride and the temperature, to know their influence on the yield of the obtained product and to find the optimum conditions of the reaction. The % yield of the obtained polymer is calculated by a simple weighing according to the following equation: yield (%) = $(M_0/M_1).100$

– M_0: weight of the obtained polymer;
– M_1: weight of the initial monomer.

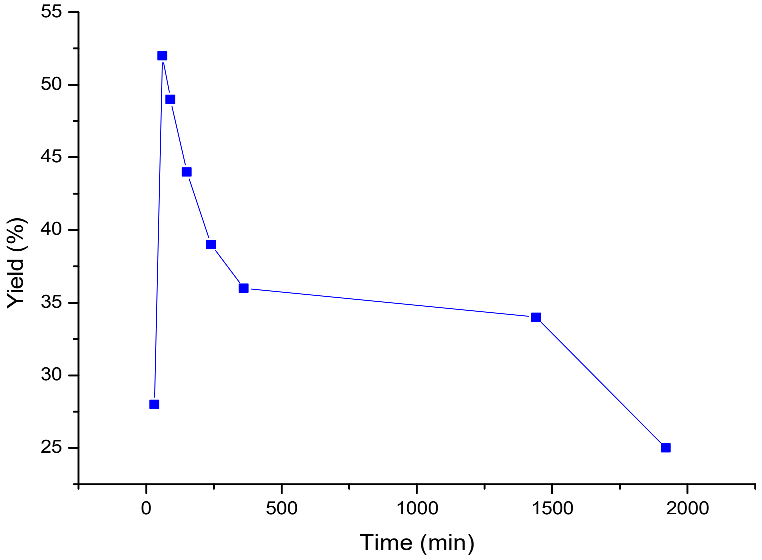


Fig. 8. Effect of time on polymerization efficiency

3.3.1. Effect of time on the yield of polymerization

We have carried out a bulk polymerization series of 1,3-dioxolane with benzoic anhydride (5 wt. % relative to the monomer), catalyzed by Mag-H$^+$ (3 wt. % relative to the monomer) at a temperature of 25 °C, varying only the reaction time. The obtained results are presented in Fig. 8. The figure shows that the polymerization proceeds rapidly within the first 60 minutes, reaching a maximum yield of approximately 52.5 %. Beyond this point, the polymerization rate decreases significantly. This behavior can be attributed to the typical characteristics of bulk polymerization systems. As the polymer chains grow, the viscosity of the reaction medium increases considerably, which limits the mobility of the reacting species and hinders efficient heat dissipation of the exothermic polymerization reaction. This interpretation confirms the influence of reaction time on the yield under the given conditions and highlights the physical limitations encountered in bulk polymerization at room temperature.

3.3.1. Effect of catalyst amount on the yield of polymerization

It is known that the catalyst amount plays a very important role in the reaction efficiency. It was chosen according to the results previously optimized. Approximately 5.3 g of monomer was added to 5 % of benzoic anhydride; the mixture was stirred at 1 hour at 25 °C. The obtained results are shown in Fig. 9.

The figure illustrates the evolution of the polymerization yield as a function of the amount of Mag-H$^+$ catalyst, expressed as a percentage relative to the weight of the monomer. The yield increases progressively with increasing catalyst amount, reaching a maximum of approximately 52 % at 3 % of Mag-H$^+$. Beyond this optimal concentration, the yield begins to decline despite the higher amount of catalyst introduced into the reaction mixture. This result suggests that while increasing the catalyst concentration initially enhances the polymerization rate by providing more active acidic sites to initiate chain growth, excess catalyst can lead to undesired side effects. One possible explanation is the occurrence of chain transfer reactions or premature termination, which are promoted by the abundance of acidic sites when the catalyst is overly concentrated. Such conditions can result in shorter polymer chains or the formation of oligomers, ultimately reducing the overall yield. Furthermore, at high catalyst loadings (above 10 %), the yield tends to plateau, indicating that the reaction reaches a saturation point where additional catalyst does not contribute significantly to further polymerization. In this regime, Mag-H$^+$ behaves more like a catalytic support, providing a stable acidic surface without proportionally increasing the number of effective catalytic events. These observations highlight the importance of optimizing catalyst concentration to balance activity and control over polymer structure and yield.

3.3.3. Effect of Benzoic Anhydride on the yield of polymerization

A series of polymerizations was carried out by studying the evolution of the yield as a function of the quantity of Benzoic Anhydride (AB), while fixing the other parameters: monomer (5.3 g), Mag-H$^+$ (3 wt. %), time (1 h), and temperature (25 °C).

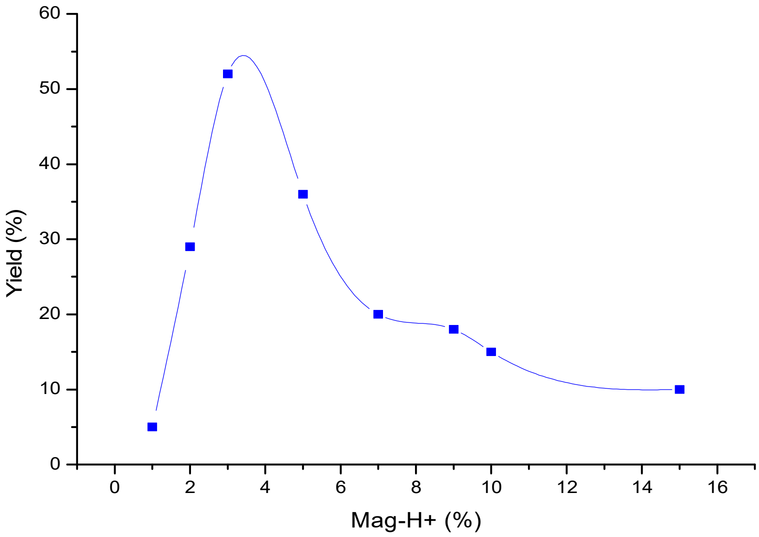


Fig. 9. Effect of catalyst amount on polymerization efficiency

The shape of the curve shows that the yield reaches a maximum value of 52 % at 5 wt. % (relative to the monomer weight) of benzoic anhydride and then decreases with the increase of the percentage of benzoic anhydride. However, as the concentration of AB exceeds 5 %, the yield begins to decline. This decrease can be explained by several competing effects. First, excessive AB may act as a chain transfer agent or react with active centers, leading to premature termination of polymer chains and the formation of low molecular weight oligomers. Second, a high concentration of AB could interfere with the accessibility of monomers to the catalytic sites of Mag-H^+, especially in a bulk system where viscosity may increase. Additionally, an excess of AB might alter the polarity or acidity of the medium, disrupting the delicate balance required for optimal cationic polymerization. Therefore, these results suggest that 5 % benzoic anhydride represents the optimal concentration under the given conditions, maximizing polymer yield while minimizing side reactions. Beyond this threshold, the negative effects of AB on polymerization kinetics outweigh its beneficial role, emphasizing the importance of optimizing co-monomer or additive concentrations in functional polymer synthesis.

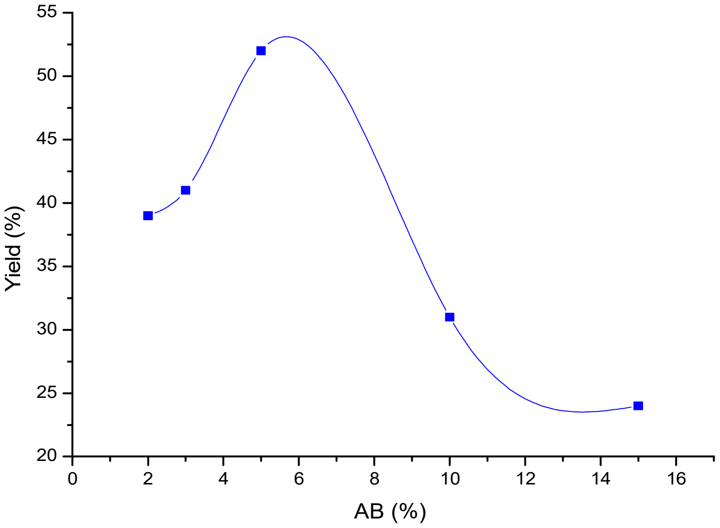


Fig. 10. Effect of benzoic anhydride ratio on the yield of polymerization

3.3.4. Effect of temperature on the yield of polymerization

Fig. 11 shows the effect of temperature on the yield of the polymerization. This study is carried out at different temperatures: 0, 15, 25, 35, and 45 °C, for 1 h with 3 % wt. of Mag-H^+. An interesting result is that Mag-H^+ initiates 1,3-dioxolane with benzoic anhydride polymerization even at low temperature in bulk. The results show that the polymerization yield increases with temperature up to 25 °C, where it reaches a maximum value of 52 %. This increase can be attributed to enhanced molecular mobility and higher collision frequency between reactive species at elevated temperatures, which facilitate the initiation and propagation steps of the cationic polymerization. At this temperature, an optimal balance is achieved between reaction kinetics and catalyst performance, resulting in maximum yield. However, the yield decreased with the temperature rising from 35 to 45 °C. It is noted that the temperature has a great influence on the yield.

These findings confirm that temperature plays a crucial role in controlling the polymerization efficiency. The data indicate that 25 °C represents the optimal condition for this system, where the catalytic activity of Mag-H^+ and the polymerization kinetics are ideally balanced to maximize yield while minimizing side reactions.

4. Conclusions

Direct functionalization of poly(1,3-DXL)with benzoic anhydride was carried out in a single step using a local catalyst, the Mag clay exchanged with protons that stands out from the others catalysts by the following characteristics: natural and ecological, less expensive, initiates polymerization reactions under mild conditions, reduces reaction time, the procedure of manipulation and purification is simpler, and the catalyst is easier separated from the reaction mixture. This method allowed us to have the synthesis of poly(1,3-dioxolane) functionalized with benzoic anhydride. The structure of the obtained polymers was confirmed by FT-IR spectroscopy and ^{1}H NMR spectroscopy. The molar mass was determined by UV. The study of the influence of the quantity of catalyst on the synthesis of poly(1,3-DXL) functionalized with benzoic anhydride showed us that an increase in the concentration of the catalyst causes a depolymerization. The influence of the increase in the polymerization time on the synthesis showed us that after 1 hour of reaction, the polymer becomes insoluble in the solvent. The best yield achieved is 52 % and at a temperature of 25 °C, time of 1 hour, with 3 % of catalyst and 5 % of benzoic anhydride. The use of Mag-H$^+$ as an ecological and reusable catalyst makes it possible to polymerize 1,3-dioxolane with benzoic anhydride at room temperature and without the use of solvent.

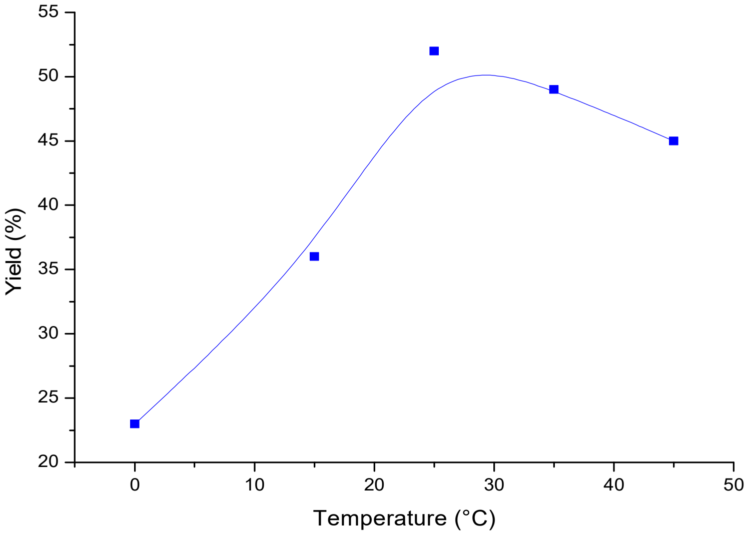


Fig. 11. Effect of temperature on polymerization efficiency

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References

[1] Nuyken, O.; Pask, S. D. Ring-Opening Polymerization – An Introductory Review. *Polymers*. **2013**, 5, 361–403. https://doi.org/10.3390/polym5020361

[2] Haque, F. M.; Grayson, S. M. The Synthesis, Properties and Potential Applications of Cyclic Polymers. *Nat. Chem*. **2020**, 12, 433–444. https://doi.org/10.1038/s41557-020-0440-5

[3] Gregory, G. L.; López-Vidal, E. M.; Buchard, A. Polymers from Sugars: Cyclic Monomer Synthesis, Ring-Opening Polymerisation, Material Properties and Applications. *Chem. Commun*. **2017**, 53, 2198–2217. https://doi.org/10.1039/C6CC09578J

[4] Draoua, Z.; Harrane, A.; Belbachir, M. Amphiphilic Biodegradable Poly(ε-caprolactone)-Poly(ethylene glycol)-Poly(ε-caprolactone) Triblock Copolymer Synthesis by Maghnite-H$^+$ as a Green Catalyst. *J. Macromol. Sci. Part A Pure Appl. Chem*. **2015**, 52, 130–137. https://doi.org/10.1080/10601325.2015.980763

[5] Du, J.; Peng, Y.; Zhang, T.; Ding, Z.; Zheng, Z. Synthesis and Characterization of pH-Sensitive Networks Containing Degradable Poly(1,3-dioxolane) Segments. *J. Appl. Polym. Sci.* **2002**, 83, 1678–1682. https://doi.org/10.1002/app.10080

[6] Yang, X.; Ye, D.; Wang, C.; Chen, Y.; Jiang, X.; Yang, Y.; Liu, Z. Simultaneously Catalyze 1,3-Dioxolane Polymerization and Construct a Hybrid Protection Layer on Lithium Anode by InF$_3$ Catalyst. *J. Power Sources*. **2024**, 600, 234262. https://doi.org/10.1016/j.jpowsour.2024.234262

[7] Ferrahi, M. I.; Belbachir, M. Cyclic Polyesters Prepared by Poly(oxypropyleneOxymaloyl) Ring-Chain Reactions. *Express Polym. Lett.* **2007**, 1, 24–26. https://doi.org/10.3144/expresspolymlett.2007.5

[8] Nabiyan, A.; Max, J. B.; Schacher, F. H. Double Hydrophilic Copolymers – Synthetic Approaches, Architectural Variety, and Current Application Fields. *Chem. Soc. Rev*. **2022**, 51, 995–1044. https://doi.org/10.1039/D1CS00086A

[9] Coenen, A. M. J.; Harings, J. A. W.; Ghazanfari, S.; Jockenhoevel, S.; Bernaerts, K. V. Formation of Cyclic Structures in the Cationic Ring-Opening Polymerization of 1,3-Dioxolane. *RSC Adv*. **2020**, 10, 9623–9632. https://doi.org/10.1039/D0RA00904K

[10] Yang, P.; Ratcliffe, L. P. D.; Armes, S. P. Efficient Synthesis of Poly(methacrylic acid)-block-Poly(styrene-alt-N-phenylmaleimide) Diblock Copolymer Lamellae Using RAFT Dispersion Polymerization. *Macromolecules.* **2013**, 46, 8545–8556. https://doi.org/10.1021/ma401797a

[11] Harrane, A.; Meghabar, R.; Belbachir, M. Kinetics of the Ring-Opening Polymerization of ε-Caprolactone Catalysed by a

Proton-ExchangedMontmorillonite Clay. React. *Funct. Polym.* **2006**, 66, 1696–1702. https://doi.org/10.1016/j.reactfunctpolym.2006.07.006

[12] Kubisa, P. Degradation of Poly(1,3-dioxolane). Depolymerization versus Hydrolysis. *Polym. Degrad. Stab.* **2023**, 72, 681–686. https://doi.org/10.1002/pi.6532

[13] Rugh, H. J.; Abdo, E. E.; Lee, J.; Kang, C.; Bem, J. N.; Balsara, N. P.; Coates, G. W. Random Copolymerization of Substituted Dioxolanes: Rational Design of High-Performance Polymer Electrolytes. *ACS Appl. Polym. Mater*. **2024**, 6, 21. https://doi.org/10.1021/acsapm.4c02928

[14] Attia, F.; Tran, T.; Bui, V.; Valluri, B.; Deng, E.; Zhang, G.; Esmaeili, N.; Huang, L.; Lin, H. Bottlebrush Polymers of Poly(1,3-dioxolane) Acetate for Membrane CO_2/N_2 Separation. *Chem. Mater*. **2024**, 36, 19. https://doi.org/10.1021/acs.chemmater.4c01679

[15] Penczek, S.; Pretula, J. Activated Monomer Mechanism (AMM) in Cationic Ring-Opening Polymerization. The Origin of the AMM and Further Development in Polymerization of Cyclic Esters. *ACS Macro Lett*. **2021**, 10, 1377–1397. https://doi.org/10.1021/acsmacrolett.1c00509

[16] Penczek, S.; Kubisa, P. Kinetics and Mechanism in Anionic Ring-Opening Polymerization. *Makromol. Chem. Macromol. Symp*. **1993**, 67, 15–42. https://doi.org/10.1002/masy.19930670104

[17] Hester, H. G.; Abel, B. A.; Coates, G. W. Ultra-High-Molecular-Weight Poly(dioxolane): Enhancing the Mechanical Performance of a Chemically Recyclable Polymer. *J. Am. Chem. Soc.* **2023,** 145, 8800–8804. https://doi.org/10.1021/jacs.3c01901

[18] Derdar, H.; Belbachir, M.; Harrane, A. A Green Synthesis of Polylimonene Using Maghnite-H$^+$, an Exchanged Montmorillonite Clay, as Eco-Catalyst. Bull. *Chem. React. Eng. Catal.* **2019**, 14, 69–79. https://doi.org/10.9767/bcrec.14.1.2692.69-78

[19] Derdar, H.; Belbachir, M.; Hennaoui, F.; Akeb, M.; Harrane, A. Green Copolymerization of Limonene with β-Pinene Catalyzed by an Eco-Catalyst Maghnite-H$^+$. *Polym. Sci. Ser. B* **2018**, 60, 555–562. https://doi.org/10.1134/S1560090418050056

[20] Elabed, Z. O.; Kherroub, D. E.; Derdar, H.; Belbachir, M. Novel Cationic Polymerization of β-Myrcene Using a Proton-Exchanged Clay (Maghnite-H$^+$). *Polym. Sci. Ser. B* **2021**, 63, 480–487. https://doi.org/10.1134/S1560090421050043

[21] Haoue, S.; Derdar, H.; Belbachir, M.; Harrane, A. Polymerization of Ethylene Glycol Dimethacrylate (EGDM) Using an Algerian Clay as Eco-Catalyst (Maghnite-H$^+$ and Maghnite-Na$^+$). *Bull. Chem. React. Eng. Catal*. **2020**, 15, 221–230. https://doi.org/10.9767/bcrec.15.1.6297.221-230

[22] Haoue, S.; Derdar, H.; Belbachir, M.; Harrane, A. A New Green Catalyst for Synthesis of Bis-Macromonomers of Polyethylene Glycol (PEG). *Chem. Chem. Technol*. **2020**, 14, 468–473. https://doi.org/10.23939/chcht14.04.468

[23] Derdar, H.; Mitchell, G. R.; Chaibedraa, S.; Mahendra, V. S.; Cherifi, Z.; Bachari, K.; Chebout, R.; Touahra, F.; Meghabar, R.; Belbachir, M. Synthesis and Characterization of Copolymers and Nanocomposites from Limonene, Styrene, and Organomodified Clay Using an Ultrasonic-Assisted Method. *Polymers.* **2022**, 14, 2820. https://doi.org/10.3390/polym14142820

[24] Baghdadli, M. C.; Derdar, H.; Cherifi, Z.; Harrane, A.; Meghabar, R. Nanocomposites by in situ Polymerization Based on Styrene-Maleic Anhydride Copolymer and Clay. *Polym. Bull.* **2023,** 80, 6869–6883. https://doi.org/10.1007/s00289-022-04392-y

[25] Bennabi, S.; Belbachir, M. Synthesis and Characterization of New Organometallic Hybrid Material LCP-1 Based on MOF (Metal-Organic Framework) and Maghnite-H$^+$, a Proton-Exchanged Montmorillonite Clay, as Catalytic Support. *J. Inorg. Organomet. Polym*. **2017**, 27, 1787–1799.https://doi.org/10.1007/s10904-017-0643-4

[26] Aiche, S. S.; Derdar, H.; Cherifi, Z.; Belbachir, M.; Meghabar, R. Activation and Characterization of Algerian Kaolinite, a New and Green Catalyst for the Synthesis of Polystyrene and Poly(1,3-Dioxolane). *Chem. Chem. Technol.* **2021**, 15, 551–558. https://doi.org/10.23939/chcht15.04.551

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СТАЛА ПОЛІМЕРИЗАЦІЯ 1,3-ДІОКСОЛАНУ, ФУНКЦІОНАЛІЗОВАНОГО БЕНЗОЙНИМ АНГІДРИДОМ: ЗЕЛЕНИЙ ПІДХІД З ГЛИНОЮ MAGHNITE-H$^+$

Анотація. *У цьому дослідженні висвітлено екологічний підхід до катіонної полімеризації 1,3-діоксолану з використанням Maghnite-H$^+$, протонованої алжирської монтморилонітової глини, як екологічно чистого, нетоксичного та економічно ефективного каталізатора. У поєднанні з бензойним ангідридом як співмономером Maghnite-H$^+$ ефективно ініціював об'ємну полімеризацію без використання традиційних токсичних ініціаторів. Умови реакції оптимізували, змінивши температуру, час, навантаження каталізатора та концентрацію співініціатора. Найвищий вихід (52 %) одержано за 25 °C через 1 годину. Отриманий полі (1,3-діоксолан) охарактеризовано за допомогою FT-IR, ^{1}H NMR та UV-Vis спектроскопії, що підтвердило успішне утворення полімеру. Термогравіметричний аналіз (TGA) показав хорошу термічну стабільність із температурою розкладу близько 300 °C. Молекулярна маса, оцінена за допомогою UV-Vis та ^{1}H NMR, становила приблизно 9700 г/моль, що свідчить про контрольовану полімеризацію. Ці результати демонструють потенціал Mag-H$^+$ як сталого альтернативного каталізатора, що підтримує екологічні стратегії в синтезі полімерів та сприяє розробленню екологічних матеріалів.*

Ключові слова: *1,3-діоксолан, бензойний ангідрид, зелена полімеризація, Maghnite-H+, характеризація.*