



Research Article

Synthesis of Polytetrahydrofuran Using Protonated Kaolin as A Solid Acid Catalyst

Abdelhak Moumen^{1,2*}, Zhour Hattab¹, Youghourta Belhocine², Kamel Guerfi¹,
Nacer Rebbani¹

¹Laboratory of Water Treatment and Valorization of Industrial Waste, Department of Chemistry,
Faculty of Sciences, Badji-Mokhtar University, BP12, 23000, Annaba, Algeria

²Department of Petrochemical and Process Engineering, Faculty of Technology,
University of 20 Août 1955 Skikda, Algeria

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Abstract

In this work, a non-toxic protonated kaolin clay exchanged with protons, was successfully applied as a solid acid catalyst for the polymerization of tetrahydrofuran (poly(THF)) at room temperature in the presence of acetic anhydride. Prior to using the kaolin as a catalyst, it was treated with HCl (0.1 M) and characterized using various analytical techniques. The amounts of catalyst and reaction time on the conversion of THF were investigated. Characterizations of nuclear magnetic Resonance of proton (1H-NMR), Fourier Transform Infrared spectroscopy (FT-IR), X-ray Diffraction (XRD), Optical Microscopy (OM), and Differential Scanning Calorimetry (DSC) techniques were used to examine the resulting polymer. X-ray characterization and DSC data indicated that the obtained poly(THF) is a highly crystalline substance. The results showed that protonated kaolin (kaolin-H⁺) has a high catalytic activity for the polymerization of THF with a conversion rate of 50.02% after 20 hours. Copyright © 2019 BCREC Group. All rights reserved

Keywords: polymer synthesis; cationic polymerization; protonated kaolin clay; polytetrahydrofuran

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1. Introduction

Many researchers have been interested in the polymerization of THF because of its industrial applications in the synthesis of plastic and fiber materials [1-8]. The polymerization can be initiated by electrophilic agents, such as: Brønsted acids (HCl, H₂SO₄, HClO₄, etc.) and Lewis acids (AlCl₃, BF₃, OEt₂, TiCl₄, etc.) [9]. However, the Brønsted acids were very harmful

protonic acids, corrosives, and expensive, while the Lewis acids required the use of a large amount. To overcome these drawbacks and to avoid the environmental pollution, the application of clean, economical, and efficient processes for the polymerization of THF requires immediate attentions. For this purpose, the use of non-toxic heterogeneous catalysts instead the mentioned homogenous catalysts can be an efficient solution method [10]. Regarding the application of heterogeneous catalysis for the polymerization process, over the last few decades, several research groups have valorized and applied some natural materials based on clays that have

*Corresponding Author.

E-mail: abdo_moumen@yahoo.fr (A. Moumen),
Telp: +213 7 91 89 29 95

been already used as solid catalysts for the polymerization of vinyl, heterocyclic and ester monomers [11-23]. Among these clay materials, the kaolin, a class of inexpensive and a new non-toxic cationic catalyst, exhibited much higher catalytic reactivities in different organic synthesis processes [10,24-25]. Many works have been devoted to the polymerization of heterocyclic monomers, such as: THF using clays as catalysts [22,26]. Recently, Ouis *et al.* [22] have studied the polymerization of THF using the kaolin of Tamazert (Mila, Algeria). The results of their research confirmed the high efficiency of kaolin for the THF polymerization where the conversion rate was 56% by the use of 15% of kaolin.

In the present study, a local kaolin obtained from the region of Guelma (north-eastern Algeria) is used as a solid catalyst in an attempt to enhance the process of THF polymerization. In order to reduce the reaction time and the amount of kaolin applied and to increase the conversion rate of THF by improving the catalyst acidity [27], the kaolin has been treated by HCl before its use. The kaolin used is whitish hydrothermal kaolin, much less plastic than most sedimentary clays and very refractor.

Two parameters were considered in the present study on the monomer conversion rate, the effect of the amount of catalyst and the reaction time. One of the most important advantages of the use of solid catalysts is certainly the easy separation of Kaolin-H⁺ particles from the polymer after the reaction and therefore, can be regenerated and reused [28]. The kaolin used in this work has been characterized using different analytical methods such as X-Ray Fluorescence (XRF), FT-IR, Scanning Electron Microscopy (SEM), Thermogravimetric Analysis (TGA), Brunauer-Emmett-Teller (BET) surface area, and X-ray Diffraction (XRD) [29]. The obtained poly(THF) was identified and characterized using ¹H-NMR, FTIR, XRD, OM, and DSC.

2. Materials and Methods

2.1 Materials and Reagents

The materials and reagents needed in this study were obtained from the following sources: tetrahydrofuran (THF, 99%, BIOCHIM) was distilled over CaH₂ under argon atmosphere before use; acetic anhydride (98% BIOCHIM); hydrochloric acid (37% w/w Fluka) and methanol (99%); local kaolin clay was procured from ECVE (society of ceramic) Guelma (Eastern Algeria).

2.2 Preparation of the Catalyst (Kaolin-H⁺)

Kaolin-H⁺ was prepared according to the procedure described in the literature [11], it has been washed respectively with distilled water and by H₂O₂ at 70 °C. Acid treatment by HCl (0.1 M) until saturation was achieved over 2 days at room temperature. Kaolin-H⁺ was then isolated by filtration and dried at 105 °C. This process was repeated until the disappearance of chloride ion by checking the filtrate by adding one drop of 0.1 M AgNO₃.

2.3 Catalyst and Polymer Characterization

The details of the characterization techniques of catalyst (kaolin) by different methods (X-Ray Fluorescence (XRF), Fourier Transform Infra red spectroscopy (FT-IR), Scanning Electron Microscopy (SEM), Thermogravimetric Analysis (TGA), Brunauer-Emmett-Teller (BET) surface area, and X-ray Diffraction (XRD)) were reported in our previous paper [29]. In the present paper, the chemical composition of the catalyst was determined with X-Ray Fluorescence (XRF) method using a Siemens type apparatus (SRS3000).

The chemical structure of the polymer was characterized according to the following procedure: ¹H-NMR spectra were obtained in CDCl₃ with a Bruker AC 250 spectrometer using tetramethylsilane (TMS) as an internal standard. The IR absorption spectrum was recorded by an FTIR-spectrometer THERMO SCIENTIFIC NICOLET IS 10. The value of *T_m* was measured by a DSC 822 instrument from Mehler Toledo with a heating rate of 5 °C/min under nitrogen atmosphere. The X-ray diffraction spectrum was obtained using an X'pert-PROPANalytical diffractometer. Surface analysis was examined using optical microscope of Richter type with magnifications up to G1200 equipped with a video camera type LEICA and computer-controlled.

2.4 Synthesis of Poly(THF)

Synthesis of the poly(THF) was carried out in a two-necked flask. The procedure was realized by mixing of 10 g (0.138 mol) of THF with the kaolin at different weight ratios (g/g) ranging from 1 to 10% (1, 3, 5, 8, and 10%) and 0.3 g of acetic anhydride (3% of the weight of monomer). Preliminary tests were achieved to optimize the amount of acetic anhydride in the reactional mixture. The optimal ratio of acetic anhydride was 3% of the weight of monomer. The reactions were carried out with magnetic stirring under argon at room temperature for

different reaction times (3, 5, 10, 15, 20, and 24 h). The nomenclature of polymer samples obtained from this experiment is of the following form poly(THF)_(mass fraction of kaolin)_(reaction time in h). The kaolin was recovered by simple filtration. The polymer was precipitated into an excess of cold methanol and dried under vacuum.

3. Results and Discussion

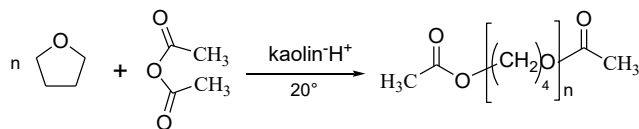
3.1 Characterization of the Catalyst

The results of the elemental analysis of used Kaolin are presented in Table 1. The kaolin consists mainly of SiO₂, Al₂O₃, and water which confirms the typical composition of hydrated aluminum silicates materials. The surface area of the kaolin treated with HCl is 56.45 m²/g. The results of the characterization of the kaolin by different methods (XRF, FTIR, SEM, TGA, BET, and XRD) were reported in our previous paper [29].

3.2 Polymerization Reaction

THF is well known to be polymerized by protonic acid, in the presence of acetic anhydride. The cationic polymerization of THF was initiated in this work using kaolin-H⁺ as a solid catalyst at room temperature; the reaction of the polymerization of THF can be summarized in Scheme 1.

The IR measurements of the product are in good agreement with the structure and composition of poly(THF) (Figure 1). Vibrations observed at 1740 cm⁻¹, 2862 cm⁻¹, and 1104 cm⁻¹ are respectively characteristic of C=O, CH, and CO groups. The vibrations at 995, 563, and 745 cm⁻¹ were attributed to the crystalline structure of poly(THF) [30]. The results deduced from the ¹H-NMR spectrum (Figure 2) confirm the structure of the poly(THF) resulting from the



Scheme 1. Polymerization of THF using kaolin-H⁺

Table 1. Elemental composition of the Kaolin of Guelma

| Oxides | SiO ₂ | Fe ₂ O ₃ | Al ₂ O ₃ | CaO | MgO | MnO | H ₂ O |
|------------|------------------|--------------------------------|--------------------------------|------|------|-------|------------------|
| Weight (%) | 43.82 | 0.20 | 36.90 | 0.23 | 0.03 | 0.025 | 18.51 |

polymerization and they adapted the results described by Ouis *et al.* [22].

Indeed the signals at 1.65 and 3.4 ppm correspond to the two groups (CH₂-CH₂-CH₂-CH₂-O), whereas those at 4.1 and 4.0 ppm correspond to the two groups (O = -CO- [CH₂CH₂-CH₂-CH₂]), and finally those at 1.92 and 2 ppm are assigned to the two methyl groups. The thermogram of the poly(THF) (Figure 3) presents a DSC endothermic peak at 39.67 °C which corresponds to the melting temperature of the product. The presence of a fine single peak during melting process indicates that poly(THF) homopolymer is highly crystalline. The crystallinity rate of the sample X_c is calculated from the relation: X_c = ΔH_m/ΔH_{m0}. Where H_m is the value of the enthalpy of melting of

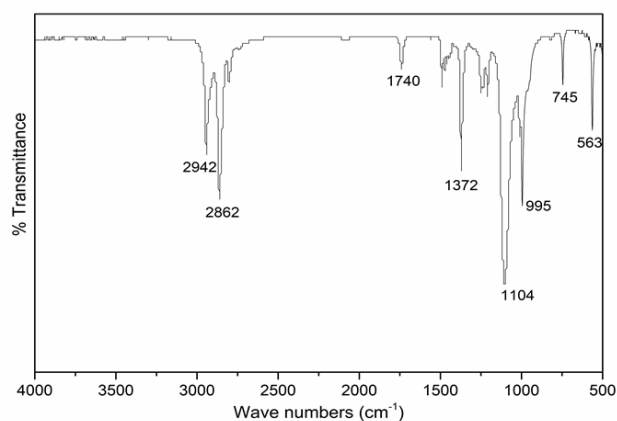


Figure 1. The FTIR spectrum of poly(THF)_{0.5_5}

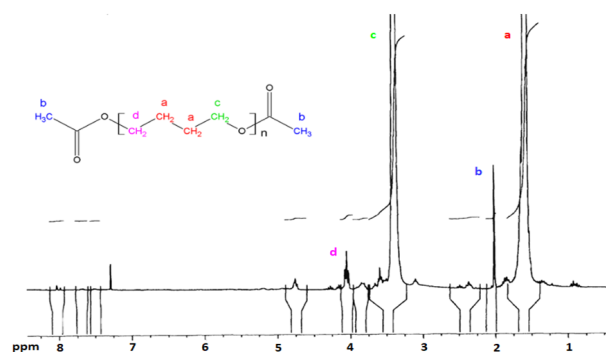


Figure 2. ¹H NMR spectrum of poly(THF)_{0.5_20}

the sample and H_{m0} the enthalpy of fusion of the polymer 100% crystalline. The literature melting enthalpy of a 100% crystalline poly(THF) sample is 175 J/g; the melting enthalpy of poly(THF) is 33.943 J/g, therefore its degree of crystallinity is 19.39%.

The X-ray diffraction provides information about the morphological state of poly(THF) polymer and its degree of crystallinity. The narrow peaks of the spectrum shown in Figure 4 confirm the good crystallinity of the poly(THF). Using the optical microscopy, a bright spherical regions indicating a semi-crystalline spherulitic morphology of poly(THF) were observed (Figure 5). The crystalline lamellae are separated from each other by the amorphous phase which appears black.

3.3 Catalyst Reactivity

The reactivity of the catalyst used in the polymerization of tetrahydrofuran was examined by studying the effect of kaolin- H^+ amount

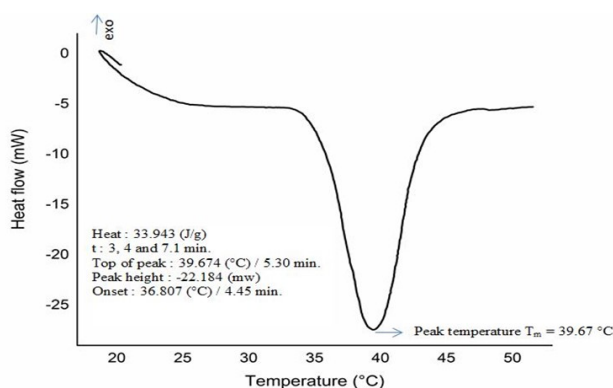


Figure 3. DSC Thermogram of poly(THF) 0.5_20 with a heating rate of 5 °C/min

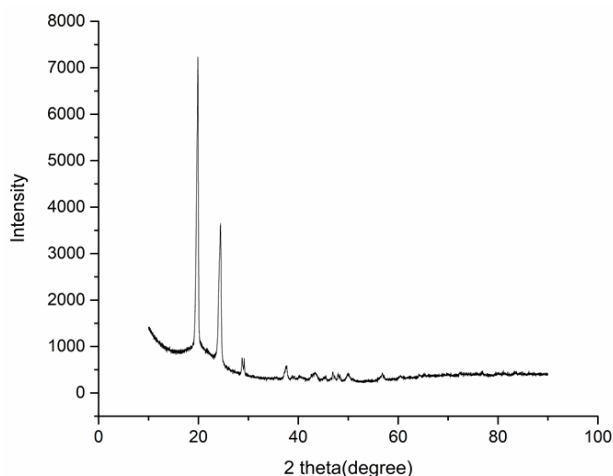


Figure 4. X-ray diffraction pattern of Poly(THF) 0.5_5

and time on the conversion of tetrahydrofuran.

3.3.1 Effect of the amount of Kaolin- H^+ on the conversion of the THF

Figure 6 shows that the variation of the weight ratio of kaolin from 1 to 10% (% of AA set at 3%) leads to an increase of the conversion rate of the monomer to the polymer. This study was carried out while keeping the amounts of the other reagents constant. When the amount of the catalyst increases, the number of active sites available for reaction is larger and therefore allows obtaining a rate of 50.02% with 8% of kaolin. However, an increase of the fraction of kaolin beyond 8% causes a sharp drop in the conversion rate from 50.02% to 10.1%. Similar results were found by Yahiaoui *et al.* [10] for the polymerization of cyclohexene oxide by Mag- H^+ and by Belmokhtar *et al.* [19] for the polycondensation of pyrrole and benzaldehyde catalysed by Maghnite- H^+ , and by Reguieg *et al.* [31] in one-step synthesis of Bis-macromonomers of poly(1,3-dioxolane) catalyzed by Maghnite- H^+ . The decrease in activity is mainly due to the difficul-

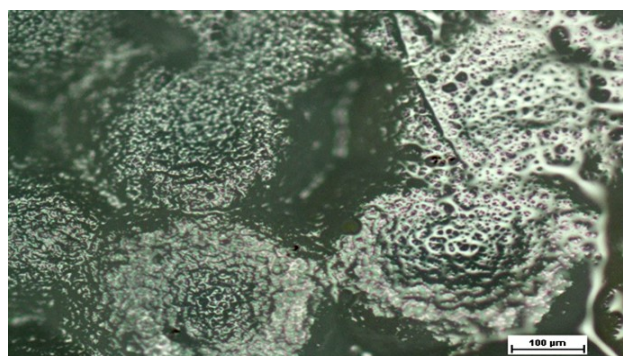


Figure 5. Optical microscopy images of poly(THF)

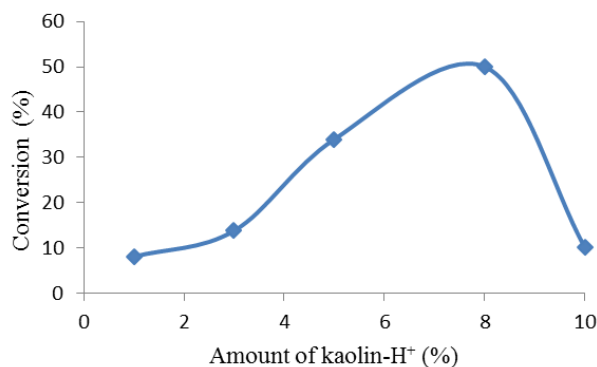


Figure 6. Evolution of the conversion of the THF as a function of the fraction of the kaolin- H^+

ties encountered by the reactants to approach and reach the active sites due to congestion. A large amount of catalyst (kaolin-H⁺) creates particle agglomerations, which reduces the total adsorption area and therefore a decrease in the catalytic activity.

3.3.2 Effect of reaction time on the conversion of the THF

The study of the influence of reaction time on the conversion rate of the THF, Figure 7 showed that the maximum yield of 50.02% is obtained after 20 hours of reaction. The initiation of the polymerization of THF is not done directly by kaolin, the presence of acetic anhydride acts as a transfer agent which makes this polymerization feasible, this process is carried out in two sub-steps:

The first step begins with the protonic addition of treated kaolin to the acetic anhydride

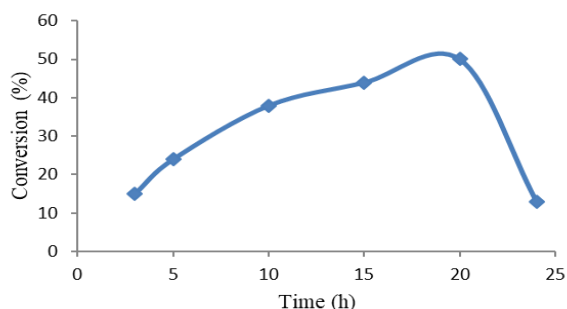
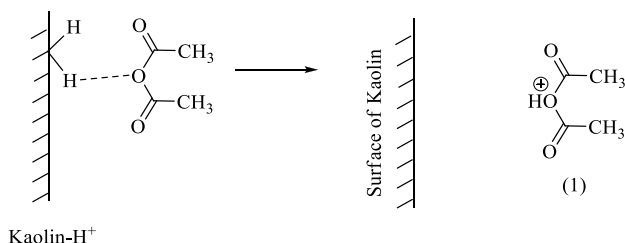


Figure 7. Evolution of the conversion of the THF as a function of reaction time with a fraction of 8% kaolin



Scheme 2. Protonation of acetic anhydride

(Scheme 2) according to the following reaction. The second step is the nucleophilic attack of the protonated acetic anhydride by a monomer molecule involving the formation of a molecule of acetic acid (Scheme 3). The propagation step would be the opening of the ring of the molecule (a) to achieve a straight chain stable energetically. The stopping of the growth of the chain is the result of the presence of the acetic acid of the initiation stage (Scheme 4).

4. Conclusion

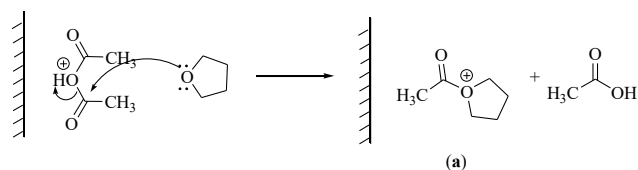
In summary, a successful synthesis of poly(THF) has been reported. The kaolin-H⁺ used in this study has proved to be an effective catalyst for the ring opening polymerization reaction of THF. The various techniques used, such as: FT-IR, ¹H-NMR, DSC, optical microscopy and XRD, show that kaolin-H⁺ initiates the polymerization process of THF by achieving 50.02% conversion rate and yields a crystalline polymer with a temperature of melting *T_m* of 39.67 °C. The optimum reaction conditions for the polymerization of THF are 8 wt% of kaolin-H⁺ and 20 hours for the reaction time.

Acknowledgement

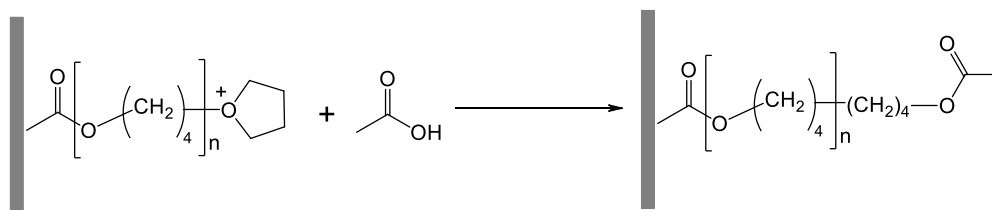
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Scheme 3. Reaction between protonated acetic anhydride and THF monomer



Scheme 4. Ring-opening polymerization reaction of tetrahydrofuran

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