Preparation and Characterization of Corn Oil Alkyd Resin Polymer under the Influence of a Catalyst and Study of its Polymerization Kinetics

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Abstract: This work involved the preparation of the polymer (alkyd resin) in two steps: the first was the preparation of monoglyceride (MG) by glycerolysis method through the reaction of glycerin and corn oil using (Pb3O4) as a catalyst at temperature of 150 °C. The second, was by condensation polymerization of the alkyd resin by polymerizing the MG prepared from the first step with a dicarboxylic acid (succinic acid (SA) in this case) in the presence of a catalyst (CaCO3) and over a range of temperatures. ˚C (210, 200, 190, 180, 170). The prepared polymer was studied and characterized using Infrared spectroscopy. Adhesiveness tests of the prepared polymers showed their solubility in water and other organic solvents, and that upon evaporation, their adhesion properties were restored. This makes these polymers potentially usable in various industries, such as the dye and paint industries. Using water as a solvent is economically superior to other organic solvents. The kinetics of polymerization reactions were studied by tracking the decrease in the acid value (AV) and the amount of water removed from the reaction medium. The energy of activation (Ea) and the parameter frequency coefficient (A) had also calculated by Arrhenius equation. The energy of activation depends on the decrease in AV found to be (Ea= -9.0456 kJ) and that depends on the amount of water removed is -8.1992 kJ . The thermodynamic functions ΔH, ΔS, and ΔG were also calculated.

1 INTRODUCTION

Alkyd resins are defined as modified polyester with adding fatty acids. They were manufactured by using polyols, like glycerol, dicarboxylic acid or carboxylic acid anhydride [1]-[2], such as phthalic acid anhydride. They can also be defined as a type of cross-linked polyester and thermosetting plastics. 90% of them are used in liquid form for coating dishes. They are characterized by their hardness and dimensional stability even at high temperatures. They are easy to color, and are characterized by transparency, adhesive strength, and heat resistance. They are also characterized by their inability to be affected by strong acids and bases, and their low resistance to moisture. They are used as pigments in paints and the printing ink industry [3]. Alkyd resins are considered important materials for coating resins. Traditionally binders are used to bind surface coatings today, alkyd resins are used as coating compounds because of their unique properties such as hardness, durability, and abrasion resistance [4]-[5]. They can also be defined as polycondensation products between polycarboxylic acids and polyhydroxyl alcohols modified with fatty acids [6]-[7]. Alkyd resins are one of the most indispensable raw materials in the coatings and decorative paint industries. Their widespread use is due to their inexpensive raw materials and ease of manufacture. Alkyd resins are not only used in decorative paints, but are also used in air-curing paints, machine tool coatings, inks, matte and semi-gloss varnishes for wooden furniture, and materials designed to protect surfaces from environmental influences [8]. The presence of oil and glycerin as components of alkyd resins gives them the quality of being environmentally friendly compared to petroleum polymers made traditionally that pollute the environmental leading to high degradation. They received attention due to their importance as inherent non-toxic nature and biodegradability [9]. Usually, oils or fatty acids used in the manufacture of alkyd resins are derived from natural sources such as flax, sunflower, coconut, bitter almond, soybean, corn, palm, cotton and other natural oils that have long chains for the manufacture of polymeric resins such as alkyds depending on the nature of the unsaturated fatty acids that present. The fatty acids included in the composition of alkyds give them flexibility, which makes them used in the manufacture of flexible coatings [10].

2 EXPERIMENTAL PART

During the synthesis and characterization of corn oil-based polymers, the following equipment was used to control reaction parameters, measure properties, and ensure accuracy:

A) Equipment used.
  1) FTIR spectrometer.
  2) Magnetic stirrer bath heater.
  3) Electronic thermometer to control the polymerization temperature.
  4) Sensitive balance for sample weight.
  5) Ostwald capillary viscometer.

B) Materials used.
  1) Corn oil.
  2) Succinic acid (SA) from CDH.
  3) Red lead oxide (Pb3O4) from CDH.
  4) Calcium carbonate (CaCO3) from CDH.
  5) Methanol (BDH).
  6) Sodium hydroxide (NaOH) from Fluka.
  7) Nitrogen gas (N2) from Iraq.

3 METHOD

The synthesis of corn oil-based polymers was carried out in two sequential steps.

Step 1. Glycerolysis reaction: In the following step, 66 ml of glycerol is added, along with (33 ml) of commercial corn oil and the catalyst of 0.3 g of red lead oxide (Pb_3O_4). These are placed in a 250 mL glass beaker and stirred at 150 °C for 5 hours, according to Figures 1 and 2, a separating funnel were used to separate the products that left over night to get a clear separated two layers of monoglycerides (the lower part of the funnel contents) and the upper part, which IR tested reveling unreacted materials. The lower part, which represents the monomer formed, then be taken for the polymerization reaction [11], and its IR spectra shown in Figures 3-6, represents corn oil, glycerin, the monomer monoglysride (MG) and the prepared polymer.

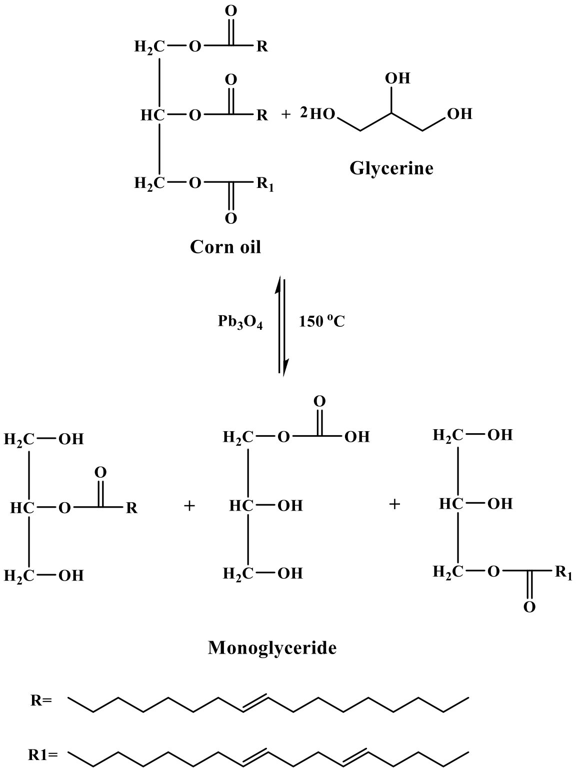


Figure 1: Stepwise glycerolysis reaction.

Step 2. Polymerization: in this step, the separated monoglyceride (monomer) from the separating funnel reacts. Then a 20 g of succinic acid (SA) as a monomer added to 50 ml of monoglysride as a seconed monomer (MG) and 0.3 g of the catalyst (red lead oxide (Pb3O4). These are placed in a three-hole glass flask, at different temperatures (170, 180, 190, 200, 210 °C), with a 10 °C interval for each experiment. Continuous stirring is carried out using a control unit (electronic thermometer) connected to the heater. High-temperature-resistant glass wool is used to maintain the reaction temperature. The polymerization process is carried out in the absence of oxygen in the presence of nitrogen gas (N_2) (an inert atmosphere). The benefit of an inert atmosphere is to prevent the reaction mixture from oxidation and to prevent the burning and blackening of the formed polymer [12] as shown in the following reaction Figure 2.

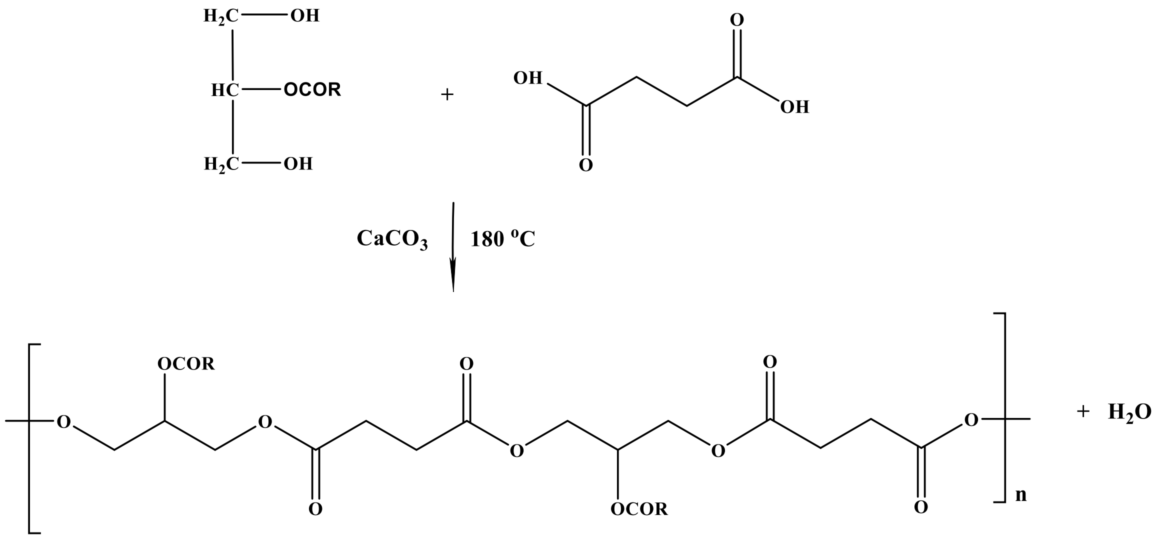


Figure 2: Stepwise glycerolysis reaction.

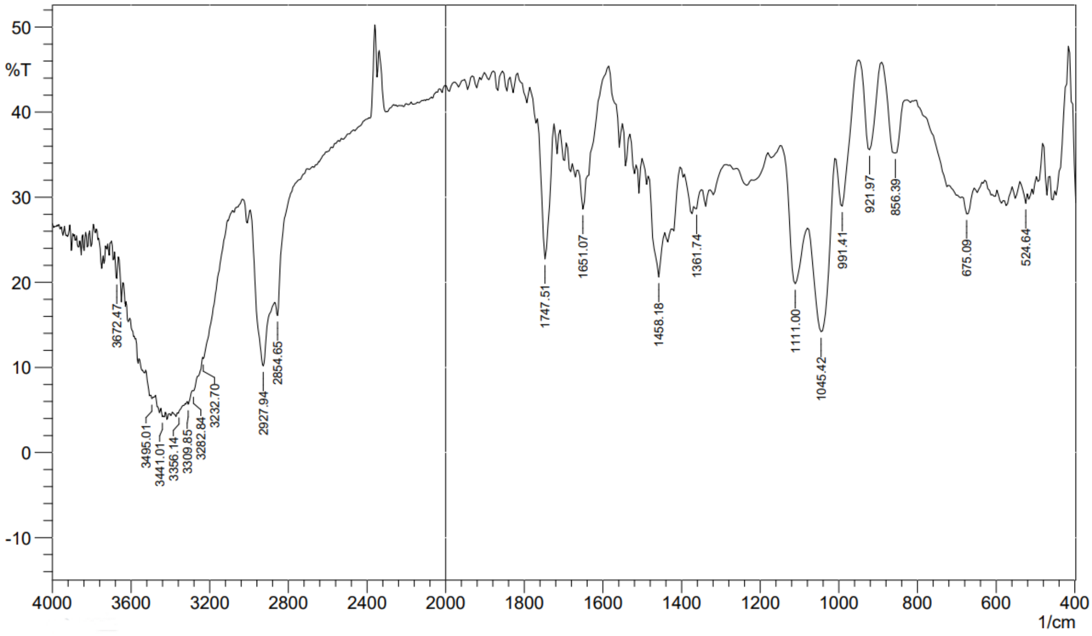


Figure 3: IR spectrum of the corn oil.

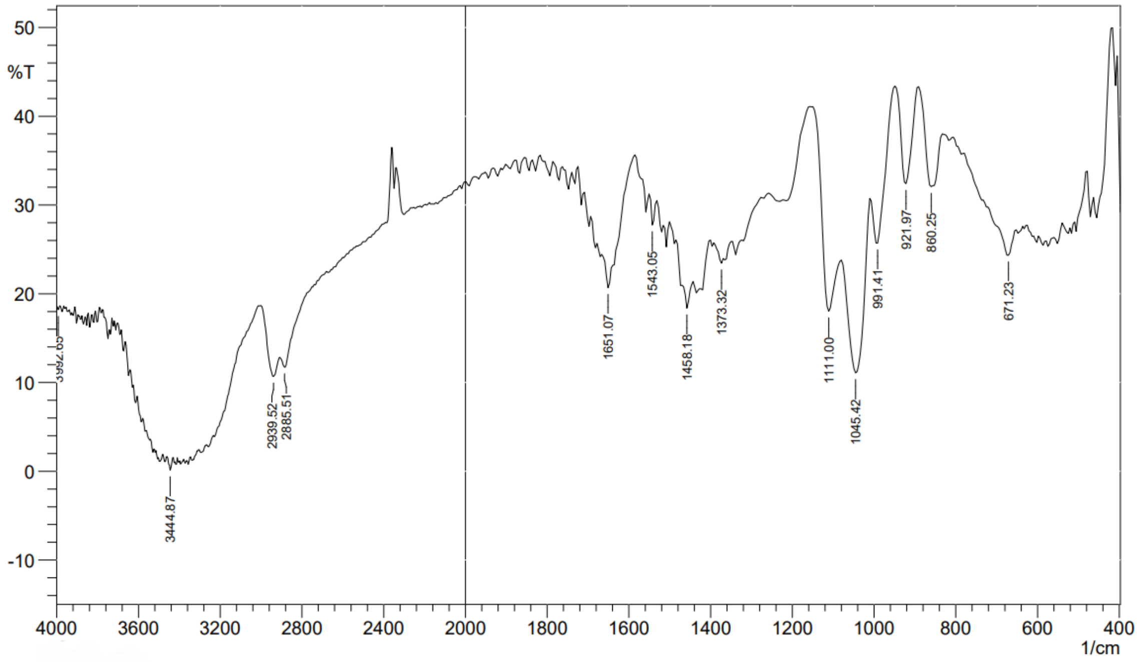


Figure 4: IR spectrum of Glycerin.

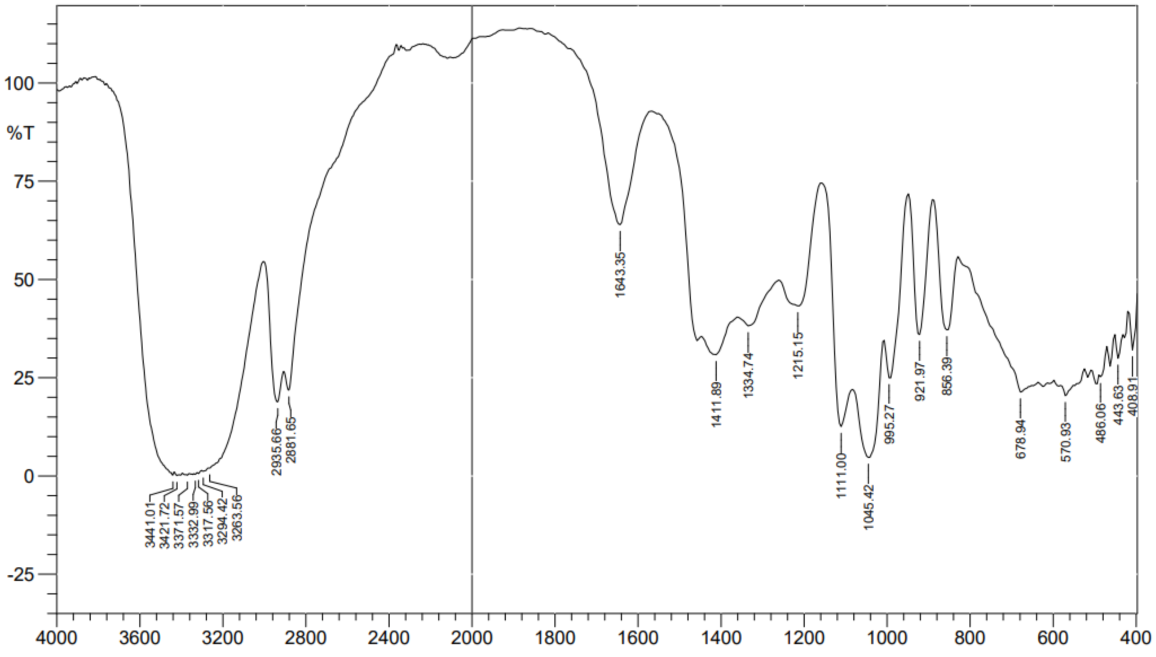


Figure 5: IR spectrum of monoglyciride (MG).

4 RESULTS AND DISCUSSION

4.1 Polymer Identification

FTIR Analysis: The prepared polymer was characterized using FTIR techniques, where absorption bands at 3421 cm^{-1} were related to vibrational stretching frequency of the (O-H) group bond, two stretching bands for asymmetric stretch at 2939 cm^{-1} and symmetric stretch at 2885 cm^{-1} were related to the normal aliphatic bond as (C-H). The band at the frequency 1662 cm^{-1} which related to the vibrational stretching of (C=O) bond, and two absorption bands at frequencies (1041 cm^{-1}) and (1238 cm^{-1}) were related to the (C-O) bond [13] As shown in Figure 6.

4.2 Reaction Kinetics by Tracking the Decrease in the Acid Value of the Polymer

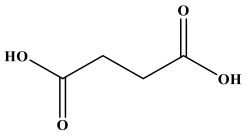
The reaction was conducted at different temperatures and with an interval of 20 minutes between readings of the prepared polymer. The acid value decrease was determined by the (1):

$$Acid\ value = \frac{V_{NaOH} \times N_{NaOH} \times 40}{Weight\ of\ Polymer}\ . \qquad (1)$$

Where: ((Acid value represents the acid value, ((V represents the volume of sodium hydroxide coming down from the burette, and N)) represents the concentration of sodium hydroxide (0.1M), (40) represents the molecular weight of (NaOH), and (wp) represents (1g) of the weight of the polymer drawn during the polymerization process. The mobility of the polymer was calculated by decreasing the acid concentration (SA) in the presence of the catalyst ($CaCO_3$) [14]-[15]. As shown in the following Figure 7.

4.3 Reaction Kinetics by Tracking the Amount of Water Removed from the Polymer

The reaction was conducted at different temperatures, with a 20-minute interval between readings, and using the catalyst (CaCO3), as shown in Figure 8.



succinic acid

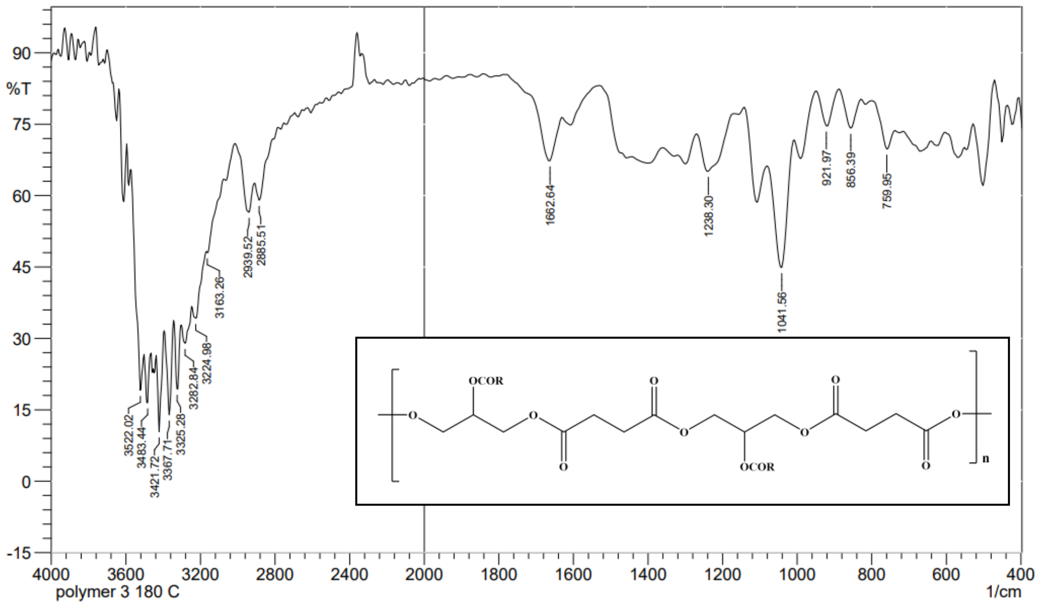


Figure 6: IR spectrum of the polymer prepared from the reaction of (SA) and (MG) in the presence of the catalyst (CaCO3).

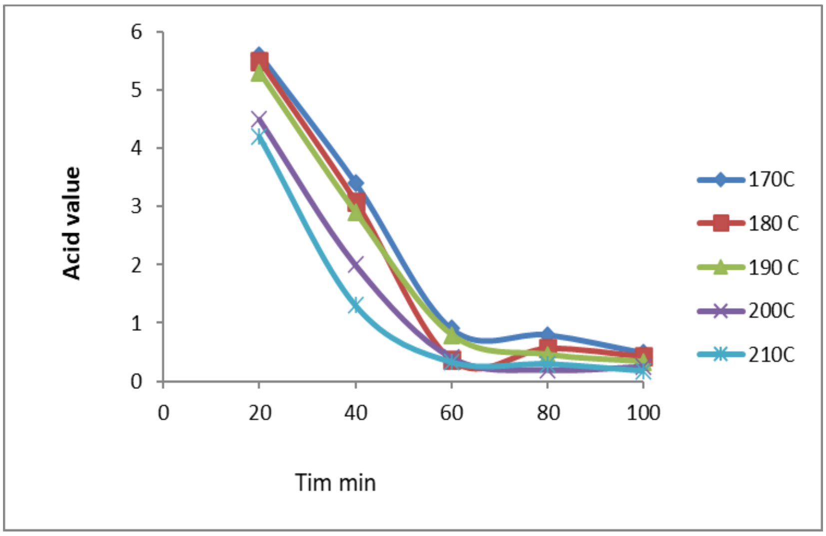


Figure 7: Reaction rate of polymerization at temperatures (200, 180, 170, 190, 210°C) in the presence of (CaCO3).

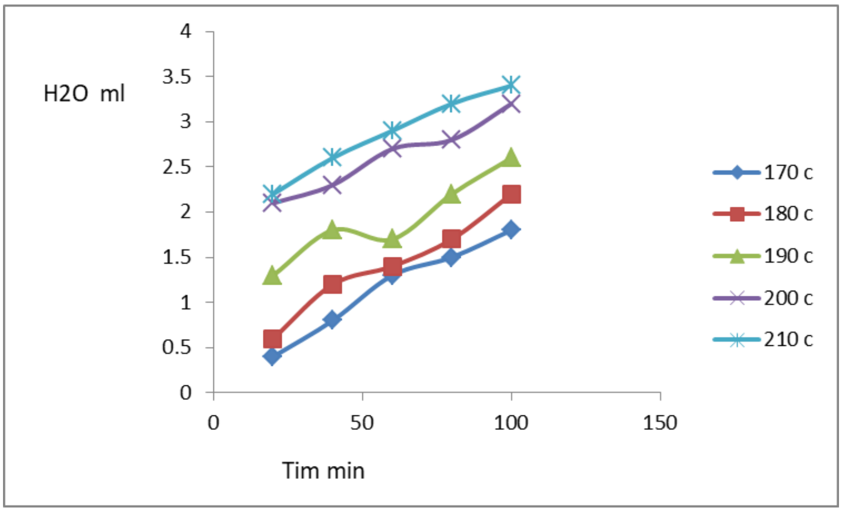


Figure 8: The rate of polymer preparation from the amount of eliminated water versus time at temperatures of 170, 180, 190, 200, 210°C in the presence of (CaCO3).

4.4 Calculating Activation Energy

The results were processed using the following Arrhenius (2):

$$k = Ae^{-Ea/RT}. \quad (2)$$

Taking the natural logarithm (ln) of both sides of the (3), it becomes:

$$lnk=lnA-\frac{E_a}{RT} \quad (3)$$

The activation energy was calculated through the curves represented in Figures 9 and 10, where (k) represents the reaction rate and was obtained by tracking the decrease in acid concentration with time as well as by tracking the amount of water removed with time. Ea represents the activation energy (E_A) in (kJ) units and a is a factor of frequency in s^{-1} units and T represents the absolute temperature in units of Kelvin (K). It was calculated from the following relationship.

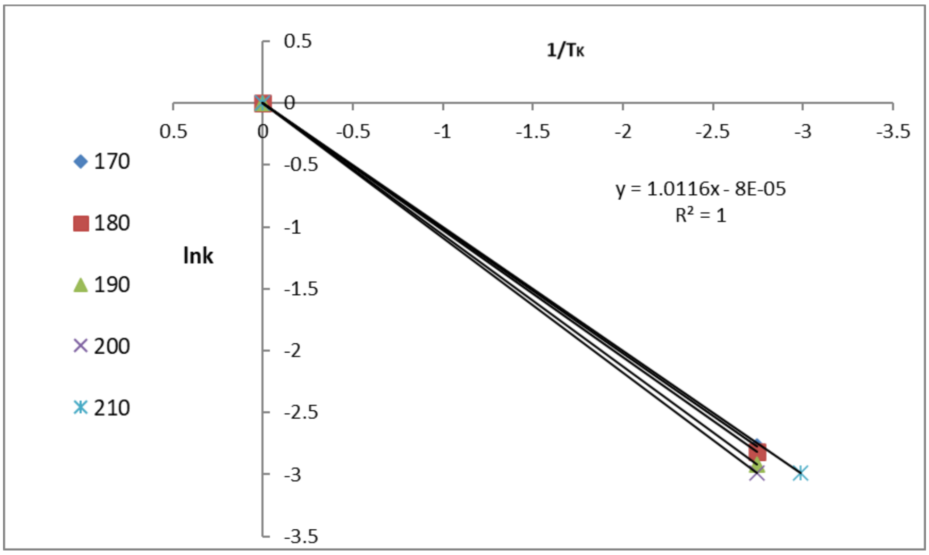


Figure 9: Graphical representation of 1/T(K) vis lnk of the polymerization reaction based on decrease of acid value in the presence of (CaCO3) as a catalyst.

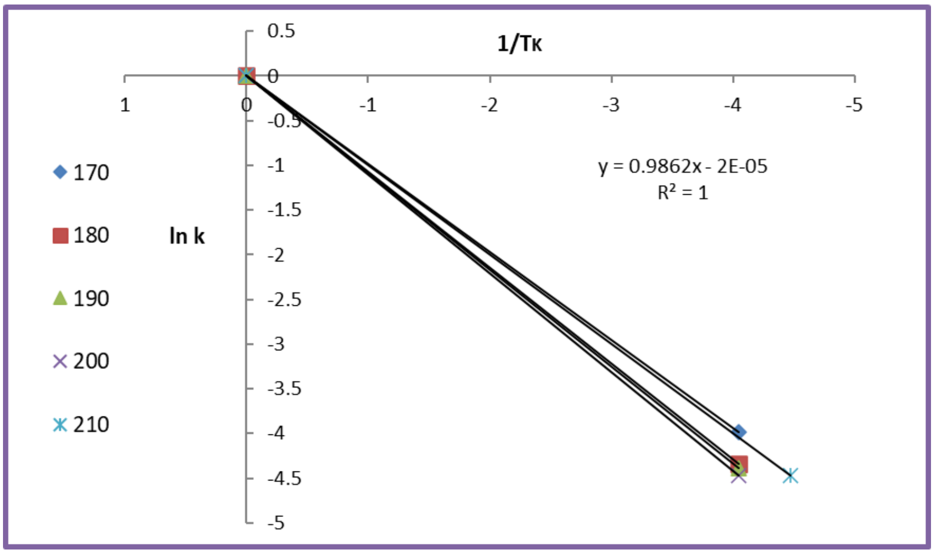


Figure 10: The graphic representation of 1/T vis lnk for the polymerization reaction based on the quantity of water elimination in the presence of CaCO3.

Table 1: The functions (ΔH, ΔS, ΔG) of the polymer in the presence of (CaCO3) as a catalyst.

T °C	TK	ΔH kJ.mol^{-1}	ΔG kJ.mol^{-1}	ΔS kJ.mol^{-1}. K^{-1}
170	443	=0.009	10.110	=0.00000332
180	453		10.458	
190	463		10.828	
200	473		11.463	
210	483		11.994	

4.5 Calculating the Thermodynamic Functions (ΔH°, ΔS°, ΔG°)

The thermodynamic functions of the first polymer P1 were calculated in the presence of the catalyst (CaCO3) and based on the decrease in acid value and using the equation of Van’t-Hoff for the graph from the calculation of the Arrhenius equation for the Figures 9 and 10. The value of (ΔH) is calculated from graph slope and the value of the entropy change (ΔS) is calculated from graph intercept when applying the Van’t-Hoff. As shown in Figure 9.

$$\frac{\Delta S^{\circ}}{R} + \ln k = \frac{-\Delta H^{\circ}}{TR}. \quad (4)$$

$$Slope = \frac{-\Delta H^{\circ}}{R}. \quad (5)$$

$$Intercept = \frac{\Delta S^{\circ}}{R}. \quad (6)$$

Where R is the constant of universal gas (8.314 J/mol.K), T is the absolute temperature in Kelvin (K), and k is the rate constant of reaction. The free energy of the reaction (ΔG) was calculated from the following (7):

$$\Delta G^{\circ} = -RT\ln k. \quad (7)$$

As shown in the following Table 1.

5 CONCLUSIONS

The study demonstrated that temperature has a significant impact on the reaction rate during polymer preparation, underscoring the importance of thermal control in polymerization processes. Water-soluble polymers can be obtained, which has positive economic and environmental benefits by reducing reliance on harmful organic solvents. The results showed that catalysts (Pb3O4, CaCO3) have an effective impact on accelerating polymerization reactions, making them important in improving process efficiency.

The decrease in acid value and the amount of water removed from the polymerization process can be relied upon as important indicators for studying polymer kinetics. It was demonstrated that the choice of monomer used in the reaction has a significant impact on the physical and application properties of the resulting polymer, necessitating careful monomer selection to achieve the desired performance in targeted applications.

The thermodynamic functions (ΔH, ΔG, ΔS) of the polymer can be calculated in the presence of catalysts (CaCO3) by tracking the decrease in the acidity value.

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