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Synthesis And Characterization Of Poly (Glycolic Acid) By Azeotropic Polycondensation

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Abstract

Poly (glycolic acid) synthesis was achieved through azeotropic polycondensation of a Hydroxy acid (glycolic acid), in the presence of a catalyst ($SnCl_2$, $2H_2O$) and an organic solvent, xylene, at a temperature of 170°C for 10 hours under atmospheric pressure. The synthesized product was characterized using several analytical methods: Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and viscometric molecular weight measurement. FTIR analysis confirmed the presence of characteristic absorption bands corresponding to different functional groups of poly (glycolic acid). XRD analysis revealed the presence of a crystalline phase constituting approximately 26%. The molecular weight of the synthesized poly(glycolic acid) was determined to be 9300 g/mol.

Keywords: *poly(glycolic acid), polycondensation, synthesis, biomaterials.*

I. Introduction:

In recent years, there has been growing interest in biodegradable synthetic polymers. These biomaterials are used in both surgery (prostheses, sutures, etc.) and pharmacology (trapping and controlled release of active ingredients). Polymers, especially poly(lactic acid) and poly(glycolic acid), play a privileged role due to their biodegradable and biocompatible nature [1, 2]. Polyglycolide or poly(glycolic acid) is a biodegradable and thermoplastic polymer, and the simplest linear aliphatic polyester. It is generally synthesized either by condensation from an α-hydroxy acid (glycolic acid) or by ring-opening polymerization from a cyclic dimer. It is hydrophobic and soluble in organic solvents such as dichloromethane, chloroform, and THF. However, it is insoluble in methanol, ethanol, and ether. Currently, polyglycolide and its copolymers like poly(lactic-co-glycolic acid), poly(glycolide-co-caprolactone), and poly(glycolide-co-trimethylene carbonate) are widely known as materials for the synthesis of absorbable sutures and are evaluated in the biomedical field [3, 4]. Our work is dedicated to the synthesis of poly(glycolic acid) through azeotropic polycondensation of glycolic acid. This polymerization reaction is carried out at different reaction times (6h, 8h, 10h, 12h). The resulting products were characterized using various analytical methods such as infrared spectroscopy, X-ray diffraction, and others.

II. Experimental Section

II.1. Synthesis of poly (glycolic acid)

In a 500 ml round-bottom flask equipped with a cooling system and a reflux condenser, glycolic acid is introduced and dehydrated at 100°C for 2 hours. Then, tin chloride $Sn(Cl)_2 \cdot 2H_2O$ was added at a concentration of 0.5% of mass of glycolic acid along with xylene. The mixture was heated to 170°C under atmospheric pressure and inert gas (argon) for varying

reaction times (6h, 8h, 10h, 12h). The obtained viscous product is allowed to cool, then methanol is added until precipitation occurs. The product is, then, recovered by filtration and air-dried for one week.

- **Purification:** in order to purify the obtained product, the powder is ground and dissolved in chloroform. Methanol is used for precipitation, followed by air-drying to obtain a white powder.

II.2. Characterization methods

II.2.1. Fourier-Transform Infrared Spectroscopy (FTIR)

The infrared spectra of the obtained product were recorded using KBr pellets and a "SHIMADZU IRTF 8300" Fourier-transform infrared spectrometer.

II.2.2. X-ray Diffraction (XRD)

X-ray diffraction measurements were performed on an "expert prof panalytical" instrument, vertical model, with a wavelength λ = 1.540598 Å. The X-ray source is a ceramic tube with a copper band.

II.2.3. Thermogravimetric Analysis (TGA)

Thermal decomposition temperature determination is carried out using a "SETARAM/TGA92" instrument. The temperature raised from 30 to 450°C under a flow of air at a rate of 10°C/min.

II.2.4. Determination of Viscosimetric Molecular Weight

The determination of viscosimetric molecular weight was performed using a capillary viscometer (Ubbelhode tube). Solutions of different concentrations were prepared for each product in chloroform. Using an Ubbelhode tube with a viscosity constant of 0.00111 in a water bath at 30°C, we have determined the outflow time t_0 for the solvent and t for each solution. We use the Mark-Houwink relation to determine molecular weights according to the following equation:

$$[\eta] = k\, M^{\alpha}$$

In our study, chloroform is the solvent, and the values of the constants k and α are respectively 0,129.10-3, 0,82.

- Degree of polymerization (DPn)

The degree of polymerization refers to the number of monomer units in a polymer chain, characterizing the polymer's size [5].

$$M = M_0 . DP_n$$

M and M_0 : the molecular weights of the polymer and the monomer, respectively.

III. Characterization of poly(glycolic acid)

III.1. Infrared Spectroscopy (IR)

The IR spectrum of poly(glycolic acid) shown in Figure 1 indicates the presence of several functional groups, predominantly between 500-2000 cm^{-1}. The most characteristic band appears at 1750 cm^{-1}, attributed to the stretching vibration mode of carbonyl groups C=O in ester functions present in PGA. Two medium stretching bands between 2900 and 3000 cm^{-1} characterizing the (CH_2) group. Several absorption bands in the region of 1230-1000 cm^{-1} correspond to the vibration of (C-O) groups, and two other bands between 720 and 950 cm^{-1} are attributed to the (C-H) group. These absorption bands characterize the poly(glycolic acid) product [6,7].

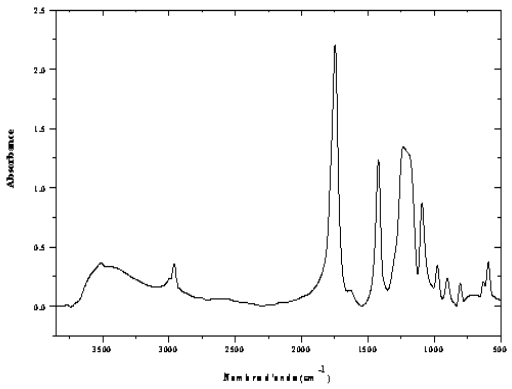

Figure 1: FTIR Spectrum of Poly(glycolic acid)

The entirety of the absorption bands of poly(glycolic acid) and their vibration modes are presented in Table 1.

Table 1: Absorption Bands of PGA and Their Vibration Modes

Frequency (cm^{-1})	**Functional Group Attribution**	**Reference (cm^{-1})**
721	δC=O	704
756	δC-H	756
800	νC-C-COO	870
969	νCH_3 + νC-C	964
1090	νs C-O-C	1100
1426	δas CH_3	1452
1750	ν C = O	1740-1790
2960	CH_2	2947-2962

3514	OH	3510

III.2. X-ray Diffraction (XRD)

The X-ray diffraction results for a sample of PGA powder, shown in Figure 2, indicate the presence of a crystalline phase characterized by two crystalline peaks. The most intense peak is located at 2θ = 28.5°, and the less intense one at 2θ = 21.9°. The crystallinity percentage of PGA is determined to be 26%.

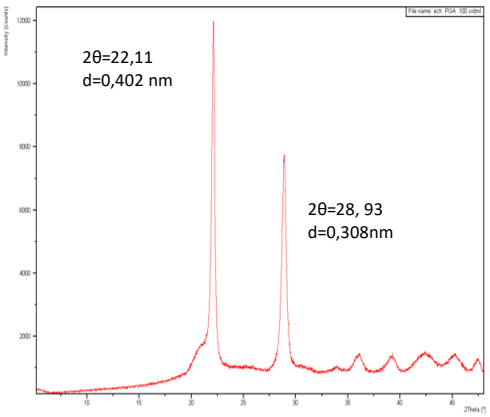

Figure 2: X-ray Diffractogram of Poly(glycolic acid)

III.3. Thermogravimetric Analysis

The thermograms presented in Figures 3 and 4 show that the degradation onset temperature for poly(glycolic acid) is 302.55°C, with a maximum mass loss rate occurring around 302.4°C.

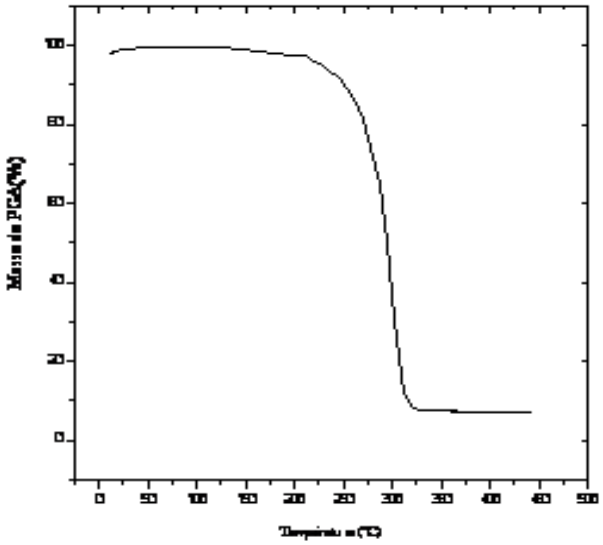

Figure 3: Mass Loss of Poly(glycolic acid) as a Function of Temperature

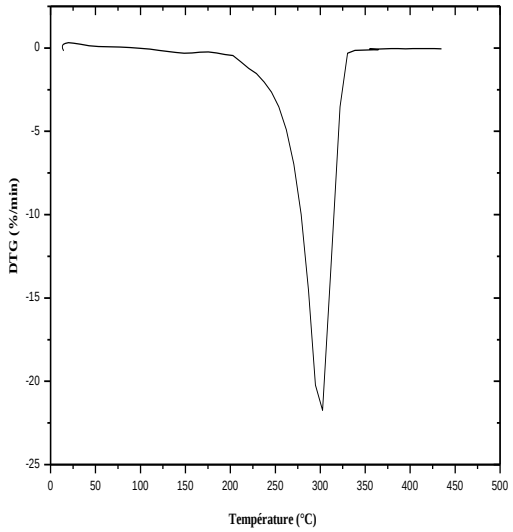

Figure 4: Degradation Rate of Poly(lactic acid) as a Function of Temperature

III.4. Viscosimetric Molecular Weight of Poly(glycolic acid)

The viscosity results of poly(glycolic acid) are presented in Figure 5, showing the curves (ηsp/c) and (Ln η_r /C) as a function of concentration.

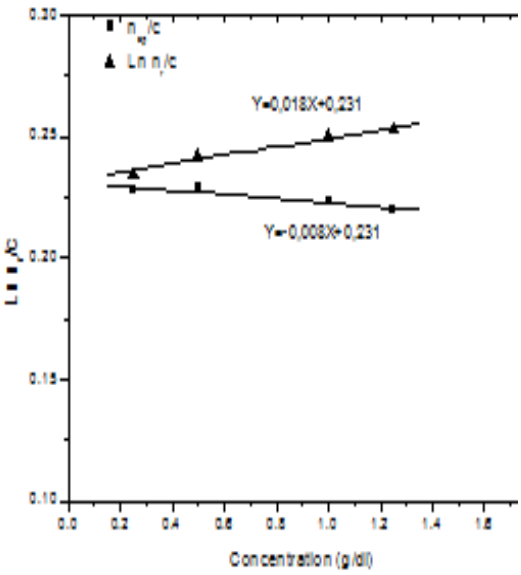

Figure5: Variation of PGA Viscosity as a Function of Concentration

The plot of ηsp/C values against concentration allows for the determination of intrinsic viscosity [η] (y-intercept). Using the Mark-Houwink relationship, the molecular weight can be calculated.

- Intrinsic viscosity [η] = 0.231
- Molecular weight M = 9300 g/mol
- Degree of polymerization DPn = 122

IV. Conclusions

Based on this study, the following conclusions can be drawn:

FTIR analysis showed the presence of all absorption bands corresponding to various functional groups of poly(glycolic acid).

X-ray diffraction confirmed the presence of crystallinity peaks in poly(glycolic acid).

Thermogravimetric analysis (TGA) demonstrated that the synthesized product exhibits thermal stability up to 302°C.

The viscosimetric molecular weight of poly(glycolic acid) is approximately 9300 g/mol.

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