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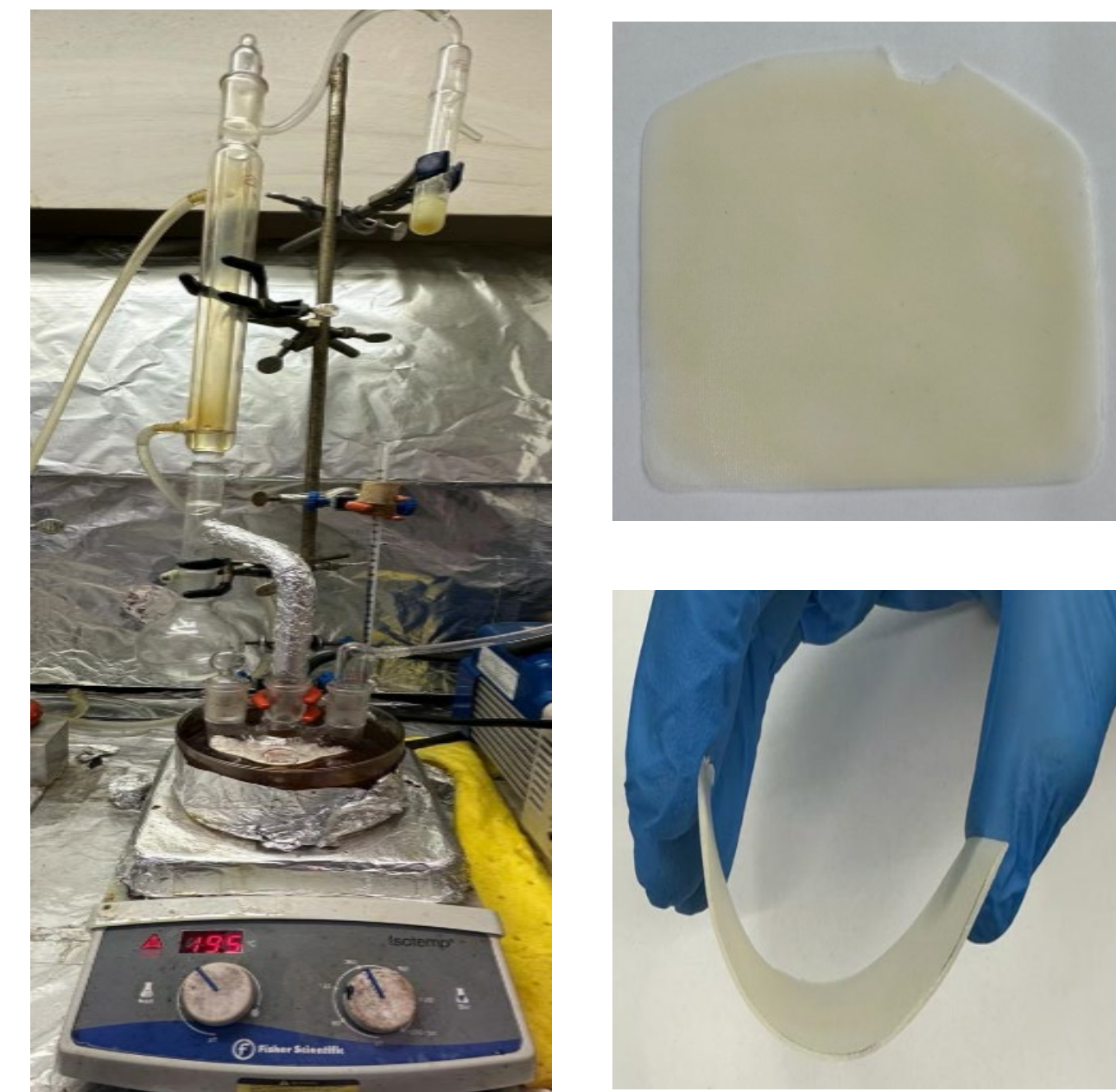
# Biobased Linear Polyester: Effect of Acids and Diols

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## Abstract

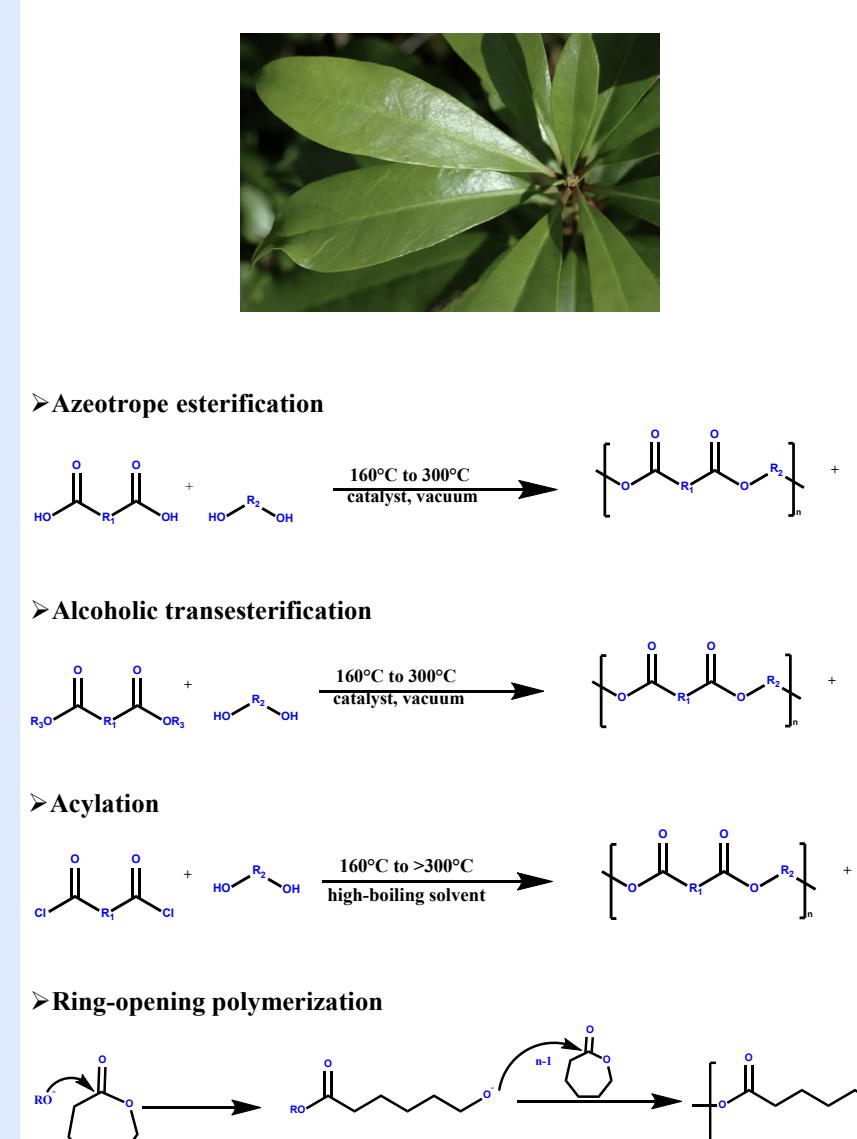
Polyester synthetics are widely used in clothing, but creating environmentally friendly materials from renewable resources is essential to reduce our reliance on non-renewable resources such as petroleum products. Azelaic acid, pimelic, and glutaric acid are natural dicarboxylic acids that can be used to synthesize bio-based polyesters. This research focuses on synthesizing saturated linear polyesters using azelaic acid, pimelic acid, and glutaric acid with diols of different carbon chain lengths. The process consists of a two-step polymerization process, which uses stannous octoate as a catalyst and hydroquinone as a radical inhibitor. The polymerization conditions, including the catalyst amount, second-stage reaction temperature, and time, were optimized to achieve a high molecular mass in the longer chain. <sup>1</sup>H NMR was used to analyze the chemical structures of the obtained polyesters. Differential scanning calorimetry (DSC) was used to explore their physical properties, including the effect of dicarboxylate chain length and long-short diol on crystalline structure and thermo-mechanical properties.



Increasing the dicarboxylic acid chain length, except for glutaric acid, increased the melting point. The glutaric acid-butane diol film was the most flexible compared to the other polyesters, reflecting good load capacity even after remolding. Overall, this research shows that it is possible to synthesize polyesters with good thermomechanical properties and film flexibility using renewable and environmentally friendly materials. These materials show promise for practical applications.

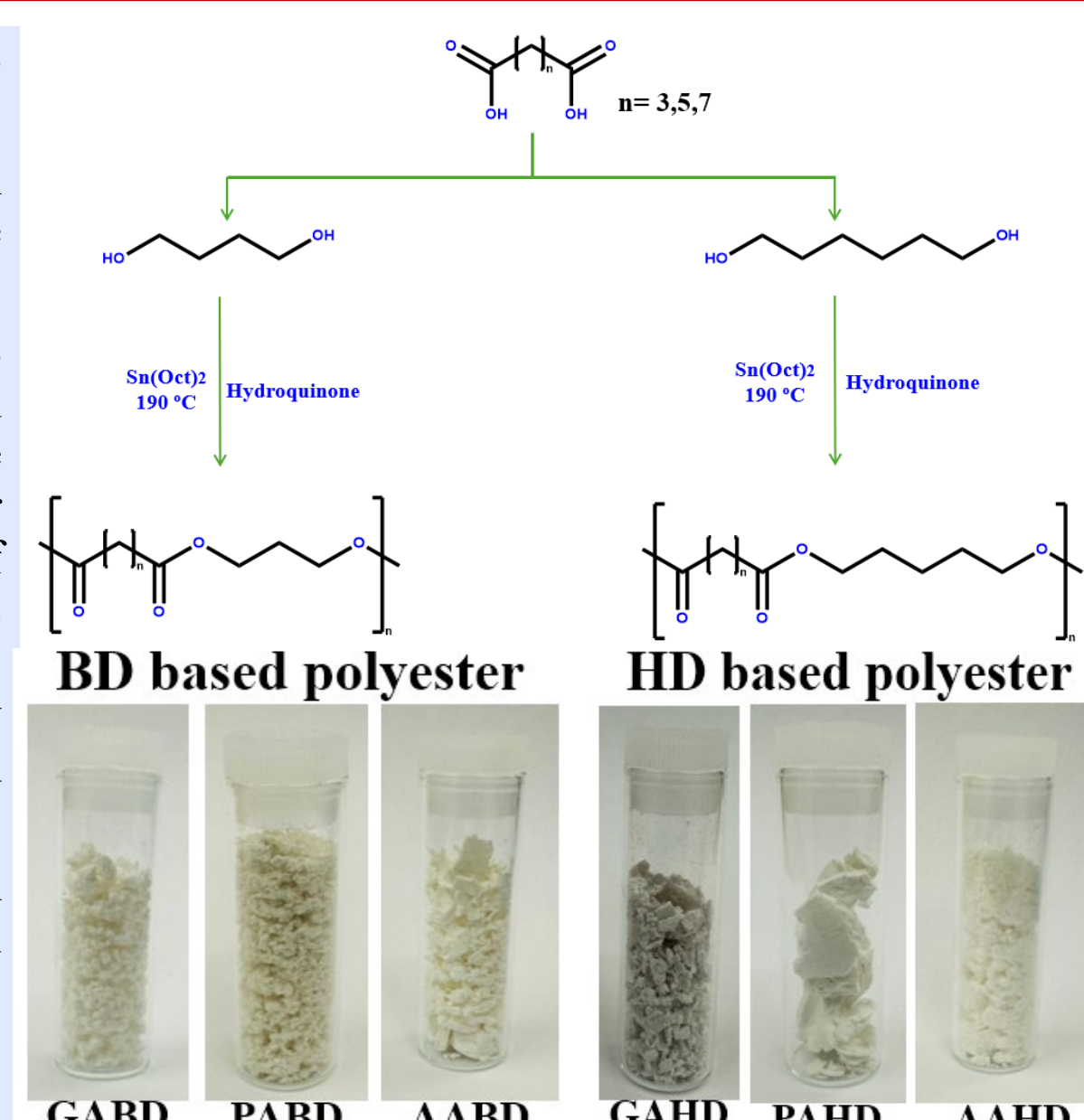
## Introduction

- Polyesters (PEs) are polymeric materials with repeating ester linkage [O-CO-R].
- Polyesters are one of the most economically essential polymers, driven primarily by PET, which is counted among commodity plastics.
- Commodity plastics or commodity polymers are plastics produced in high volumes for applications where exceptional material properties are not needed (such as packaging, food containers, and household products).
- Natural polyesters are biodegradable, but most synthetic polyesters, used extensively in clothing, are not biodegradable.
- Polyester Fiber:**
  - PET is the most common polyester used to produce fibers
  - cost-effectiveness.
  - Polyester fibers resist weather and light, abrasion, and moisture absorption.
- Polyester Resin:**
  - many advantages over other thermosetting resins, such as the ability to cure at room temperature, mechanical solid qualities, and transparency.
- Polyester Film:**
  - Optical, physical, mechanical, thermal, and chemical qualities.
  - It is mainly used for its high tensile strength, chemical and dimensional stability, transparency, and reflectivity.
- Polyester is classified into two categories:
  - Natural - Cutin component of plant cuticles
  - Synthetic - Linear, branched, aliphatic, aromatic.
    - It can be a thermoplastic or a thermoset
    - Poly (butylene terephthalate) (PBT)
    - Poly (ethylene terephthalate) (PET)



## Synthesis

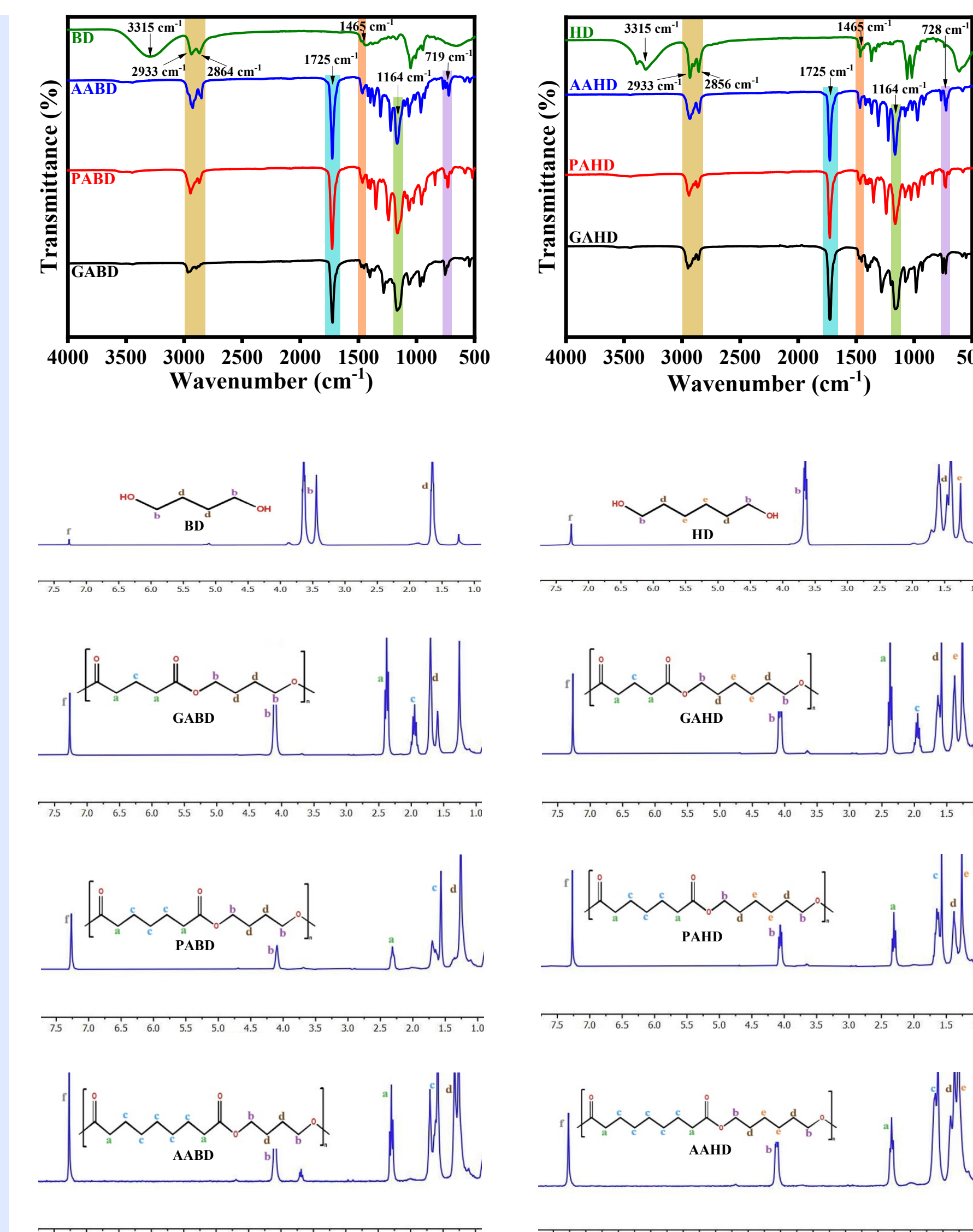
- All polyester was synthesized by two conventional two-step esterification and polycondensation.
- To create biobased polyesters, this study's synthons are based on sustainable resources and tin (II) 2-ethyl hexanoate was used as the catalyst for polymerization.
- The reactants were first treated to a reaction containing 0.25 mol% Sn (Oct)2 at 190 °C for five hours to complete the esterification process. To polymerize goods with a high molecular mass, the second step was conducted at 230 °C for 5.0 hours while under vacuum (5 Pa). To prevent potential discoloration or yellowing of polyesters due to thermal degradation, the reaction mixture's maximum temperature was limited to 240 °C. Once the reaction was complete (the Weissenberg effect was seen or the melt viscosity increased), the reaction mixture naturally cooled to room temperature.
- The resulting polyesters were purified after dissolving in chloroform and re-precipitating in methanol. The refined polymers were then allowed to dry at ambient temperature. Removing excess byproducts or diol from the reaction mixture is crucial to increasing temperature and reducing pressure (by applying a vacuum).



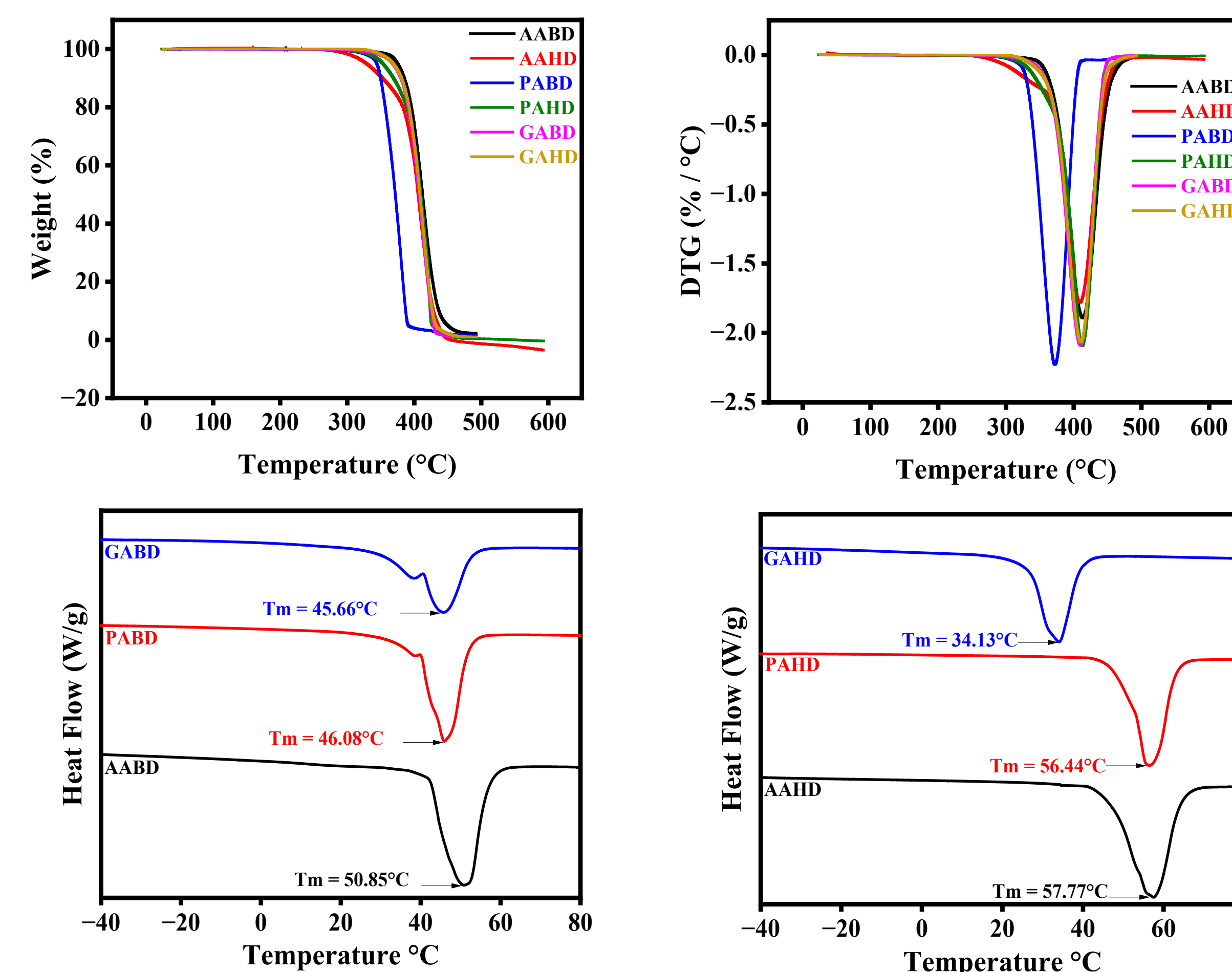
## Characterization

FTIR analysis of dicarboxylic acids like glutaric, pimelic, and azelaic acids showed structural changes indicating polyester formation. The disappearance of a peak at 1686 cm<sup>-1</sup> and the appearance of a peak at 1725 cm<sup>-1</sup> indicated the conversion of carboxylic acid to ester groups. C-O stretching vibration at 1164 cm<sup>-1</sup> confirmed diester formation. Peaks at 2932 cm<sup>-1</sup>, 2846 cm<sup>-1</sup>, and 1464 cm<sup>-1</sup> indicated the presence of -CH<sub>2</sub> groups. A peak at 716 cm<sup>-1</sup> showed a long-chain alkane presence. As chain length increased, peaks shifted but didn't significantly affect chain length.

NMR spectroscopy is crucial for identifying organic compound structures and monitoring synthesis. Samples were prepared with acids in DMSO and polyesters in deuterated chloroform. The shift in CH<sub>2</sub> peaks from 3.6 ppm to 4.2 ppm indicates polyester formation. Peaks at 2.20, 1.46, and 1.2 ppm correspond to CH<sub>2</sub> groups in specific acids, remaining stable post-reaction. Peak shifts from 1.9 ppm to 1.5-1.8 ppm with increased chain length suggest electron withdrawing effects. New peaks at 1.2-1.5 ppm appear with longer diol chains. CDCl<sub>3</sub> peaks at 7.2 ppm, while water in CDCl<sub>3</sub> merges with alkyl chains around 1.5 ppm.



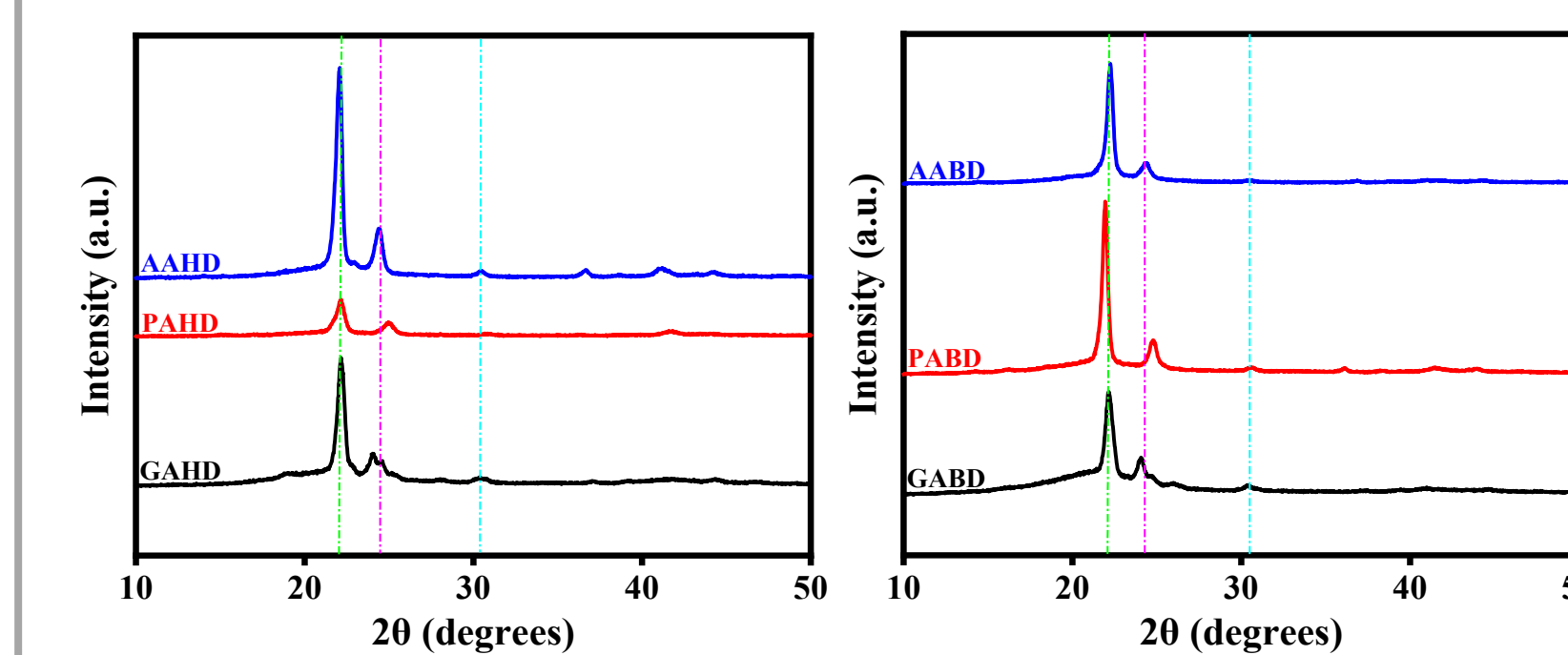
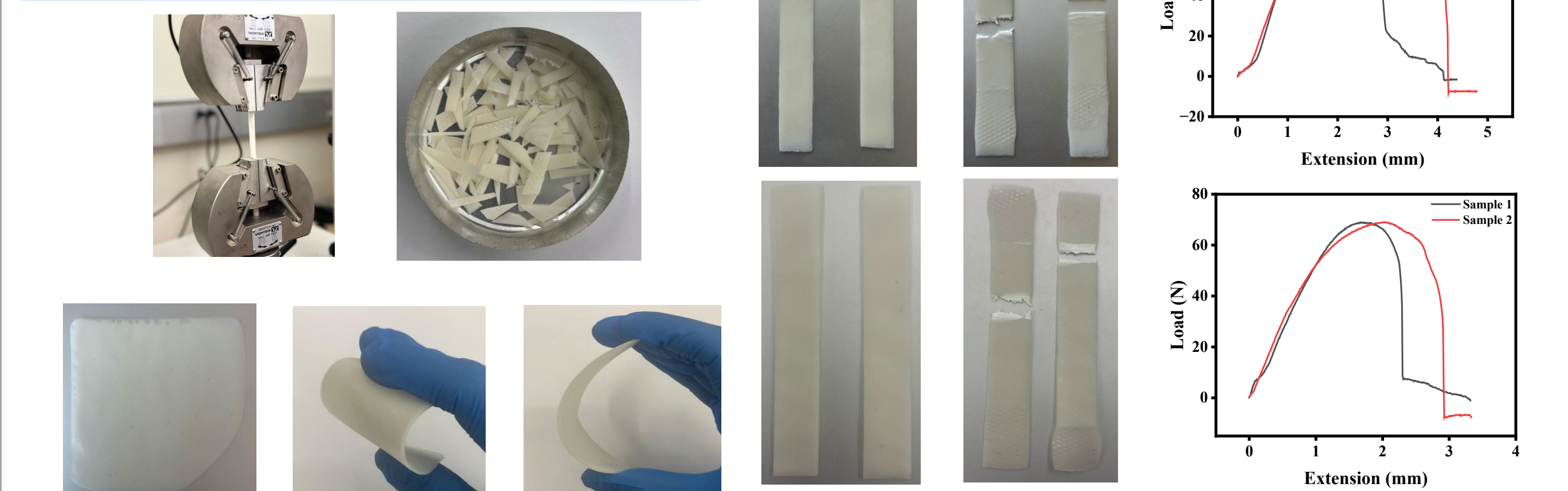
## Result and discussion



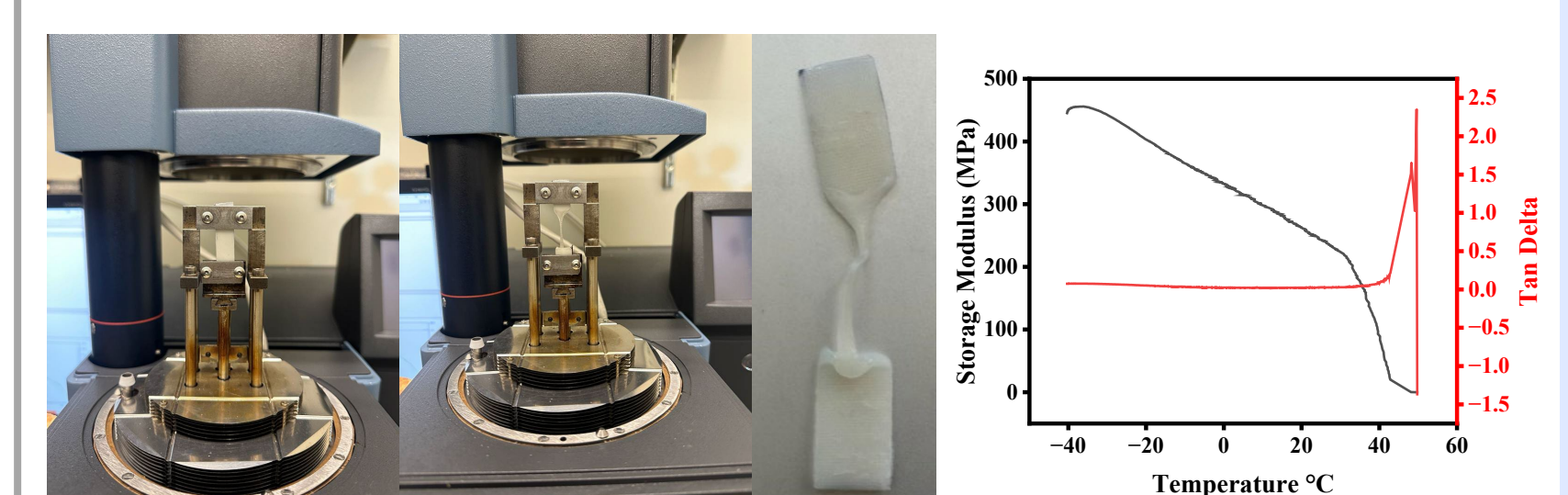
Thermal stabilities of synthesized polyesters were analyzed via TGA. AA-HD and PA-HD exhibited two-step degradation, with initial degradation at 275-364 °C and 321-371 °C, respectively, followed by significant degradation. Other polyesters showed single-step degradation from 319 to 476 °C, indicating good thermal stability. PA-BD displayed maximum loss at 370 °C, while AA-BD demonstrated the highest thermal stability with 5% weight loss at 374 °C. Increasing diol chain length, as in AA-HD, resulted in decreased thermal stability (T5% at 328 °C). The polyesters exhibited good thermal stability due to their high molecular weight and material strength.

The DSC analysis revealed that all synthesized polyesters exhibited melting temperatures (T<sub>m</sub>) ranging from 34 to 57 °C, indicating their semicrystalline nature. AA-BD, AA-HD, PA-BD, PA-HD, GA-BD, and GA-HD showed single melting points at specific temperatures. For instance, AA-BD had a T<sub>m</sub> of 50.85 °C, which increased to 57.64 °C in AA-HD with a longer diol chain. Similarly, PA-BD and PA-HD displayed T<sub>m</sub> values of 46.08 °C and 56.44 °C, respectively, following the same trend. However, GA-BD and GA-HD showed a reverse trend, decreasing T<sub>m</sub> from 45.66 °C to 34.13 °C with increased chain length.

The tensile strength of GA-BD polyester. It is recommended that one seriously consider replacing petroleum-based starting materials, which are helpful in adhesives, cables, seat belts, sealants, surgical tubes, packaging material, rubber, etc. However, bio-based linear saturated polyesters were not widely reported. So here, we tried to synthesize biobased polyesters with increasing dicarboxylic acid and diol chain lengths. The tensile of the polyester films was conducted according to standard ASTM D882. The maximum load capacity of this film ranges from 80 to 90 Newton, with an extension of up to 4 mm. The data doesn't suggest that it can compete with the current polyester that exists in the market. However, it shows good remolding capacity. The same film was cut into small pieces, and after hot pressing, an almost identical film was prepared, as shown in Figure 17. After remolding, its loading capacity was reduced by 15 N, and the extension was 2.5 to 3 mm, which indicates material stiffening on remolding.



The WAXD patterns of all the synthesized polyester crystalline structures. Peak fitting was used to examine the patterns, and the ratio of the total area of all crystalline reflexes to the area of all reflexes was used to determine the crystallinity. Similar diffraction peaks can be seen in AA-BD, AA-HD, PA-BD, PA-HD, GA-BD, and GA-HD at 22.2°, 24.4°. The planes (110) and (010) are assigned according to the observed peaks. There are also some minor familiar diffraction peaks at 30.5° and 36.06°, set to (120) and (100) planes, respectively. All the synthesized polyesters exhibit abrupt intensity peaks at 22.2° and 24.4°, indicating uniform crystallinity in all the synthesized polyesters.



DMA examined viscoelastic behavior and glass transition temperature (T<sub>g</sub>) of polyester films, with a focus on GA-BD polyester. Films tested from -40 °C to 60 °C. GA-BD exhibited good mechanical strength, allowing DMA analysis unlike brittle films. Storage modulus of GA-BD decreased from 450 MPa, notably between 35 to 45 °C. This, along with high tan δ peak, indicated material's T<sub>g</sub>. DSC confirmed T<sub>g</sub> at 45.72 °C, aligning with DMA results.

## Conclusions

Using Tin (II) 2-ethylhexanoate as the catalyst in a two-step melt polycondensation process, glutaric acid and two distinct aliphatic diols—1,4-butanediol and 1,6-hexanediol—were successfully converted into a high molecular weight biobased aliphatic polyester. Using GPC and <sup>1</sup>H NMR, respectively, the molecular weight and chemical makeup of all produced polyesters were examined. GA-BD exhibited the highest weight-average molecular weight of 48,439 g/mol and a degree of polymerization of 1.83. DSC, TGA, and WAXD were also used to describe the polyester series and learn more about the polymers' crystallinity and thermal characteristics. It's observed that T<sub>m</sub> increases with increasing dicarboxylic acid chain length. The same result was obtained with increasing diol chain length except for glutaric acid, owing to the odd-even effect of carbon chains in crystal packing. All polyesters have enough thermal stability for melt processing and are semicrystalline. GA-BD shows a storage modulus of 0.5 MPa and good remolding capacity.

## Acknowledgements

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- Pittsburg State University

## Reference

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