Bio-based and Biodegradable Superabsorbent Polymers Based on Citric Acid and Polyols

Chen, Jingying

DOI:
10.33612/diss.1155297636

Appendix A

-Supporting Information-

Figure S1. Crystal-clear solution of polyester synthesized from CA and glycerol

Explanation of different reaction mechanism in bulk or in organic solvent:

The possible mechanism is as follows: After the formation of citric anhydride, the ester bond will be formed at the less reactive tertiary carboxylic acid via the Burgi-Dunitz trajectory. The Burgi–Dunitz angle (BD angle) is the angle that defines the geometry of attack of a nucleophile on a trigonal unsaturated carbonyl center in an organic ketone, aldehyde, ester, or amide carbonyl. Precisely, in the case of nucleophilic attack at a carbonyl, it is defined as the Nu-C-O bond angle, where Nu is the atom of the nucleophile forming the bond with the carbon atom. The angle between the line of nucleophilic attack and the C-O bond is greater than 90˚. This is due to a better orbital overlap between the HOMO of the nucleophile and the π* LUMO of the C-O double bond. An example is given in **Figure S2**.

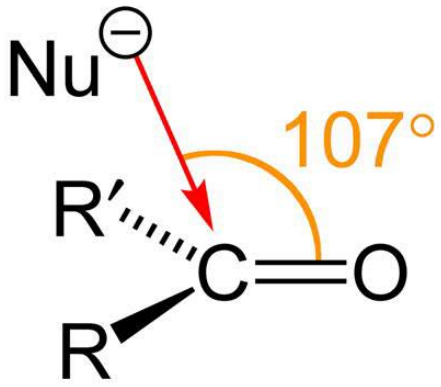


Figure S2. Shown is the nucleophilic attack by a charged nucleophile (Nu) on the unsaturated trigonal center of the aldehyde electrophile. The value computed as optimal for

this system, 107°, is indicated, and is representative of the obtuse values observed in most experimental chemical systems

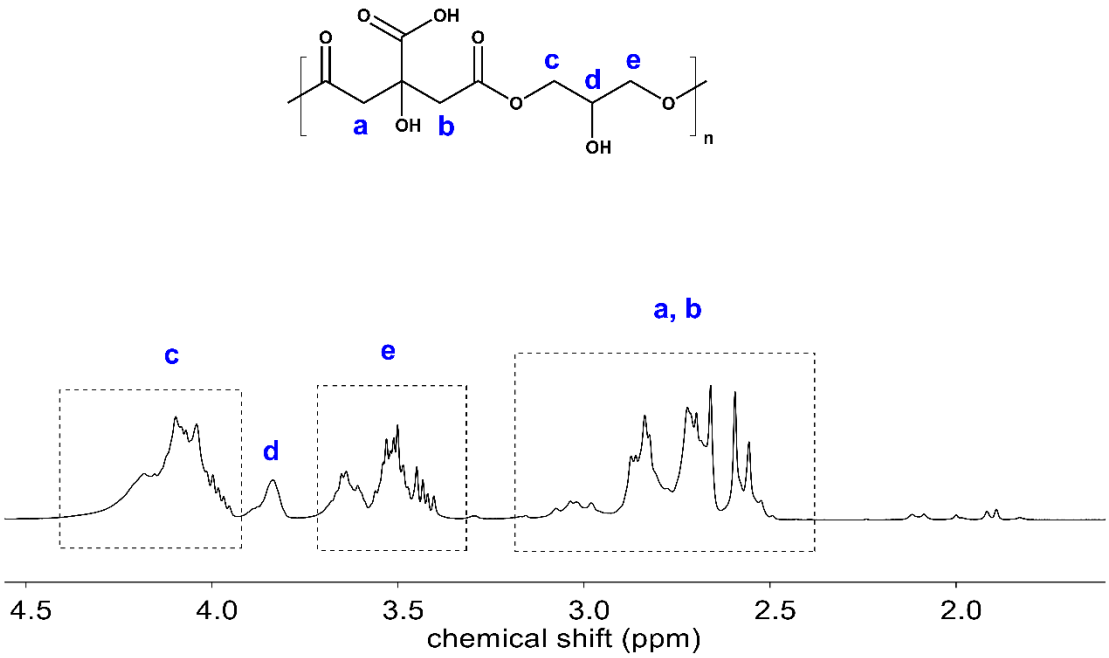


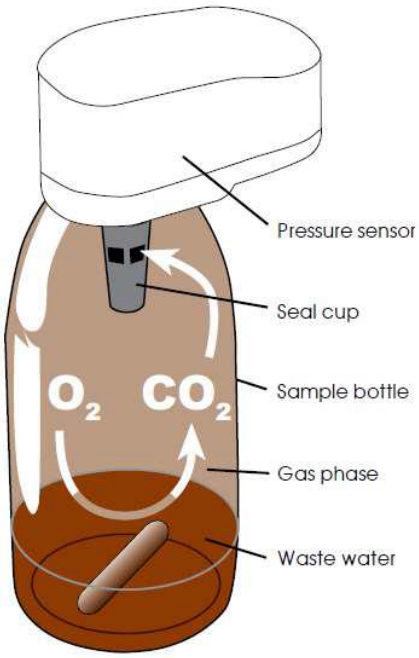
Figure S3. ^{1}H NMR spectrum of the products of the reaction between CA and glycerol. All peaks are assigned based on prediction via ChemDraw software (version: ChemDraw 20.0)

Appendix B

Biodegradation method

(Made by: Christina Lavilla Aquilar)

A pre-determined amount of the test substance is dissolved in the test medium (e.g. water containing activated sludge). The solution is kept in a closed bottle in the dark at a constant temperature, and the biodegradation is followed by measuring the biochemical oxygen demand (BOD). The BOD of a substance is an expression for the amount of oxygen consumed by the decomposition of organic matter in a biochemical process. In the closed bottle, above the sample itself, is a defined volume of air. During the BOD measurement, the bacteria in the medium consume the dissolved oxygen. This is replaced by oxygen in the bottle above the sample. This generates a decrease in pressure within the system. This is measured by the BOD sensor and displayed as BOD value in mg/L O_2. The carbon dioxide released at the same time reacts with the potassium hydroxide in the seal gasket.



Preparing the samples and performing the measurement

1) Estimate the amount of (solid) test substance that will be used.

a. First calculate the theoretical oxygen demand (ThOD) of the test substance (see e.g. Annex IV in OECD301), which will be given in mg O2/mg test substance. The ThOD of a substance $C_cH_hCl_{cl}N_nNa_{na}O_oP_pS_s$ of the molecular weight MW is calculated according to:

$$\text{ThOD}\left(\frac{mg\ O_2}{mg\ test\ substance}\right) = \frac{16[2c + 0.5(h - cl - 3n) + 3s + 2.5p + 0.5na - o]}{MW}$$

This calculation implies that C is mineralized to CO_2, H to H_2O, P to P_2O_5 and Na to Na_2O. Halogen is eliminated as hydrogen halide and nitrogen as ammonia.

Note: nitrification inhibitor can be added to the samples (see step 5b) to be sure that nitrogen is eliminated as ammonia and no nitrification takes place.

b. In principle, the volume of test medium used in each bottle is 157 mL, and the measurement range is 0-400 mg/L O2. If necessary, different measurement range and sample volume can be used (see instructions manual of AL606 biodeg equipment for further information).

c. Calculate the amount of test substance taking into account the volume of test medium and the maximum BOD value in the measurement range:

$$mg\ test\ substance = \frac{400\ mg\ O_2}{1\ L\ water} * 0.157\ L\ water * \frac{1\ mg\ test\ substance}{ThOD\ mg\ O_2}$$

2) If applicable, age the activated sludge by storing it under aerobic conditions at the test

temperature. During ageing, the content of easily degradable organic material is reduced

3) Prepare the following stock solutions:

a. Stock A: 8.50 g KH_2PO_4 + 21.75 g K_2HPO_4 + 33.30 g $Na_2HPO_4.2H_2O$ + 0.50 g NH_4Cl,

dissolve and make up to 1 liter with distilled water.

b. Stock B: 27.50 g $CaCl_2$, dissolve and make up to 1 liter with distilled water.

c. Stock C: 22.50 g $MgSO_4.7H_2O$, dissolve and make up to 1 liter with distilled water.

d. Stock D: 0.25 g $FeCl_3.6H_2O$, dissolve and make up to 1 liter with distilled water. To prevent precipitation, add to this solution one drop of concentrated HCl.

4) Add per liter of (aged) test medium 1 mL of each of the above stock solutions (A, B, C, D).

Saturate the test medium with air at the test temperature by aerating with clean compressed air for about 20 minutes.

5) Prepare groups of bottles for the determination of the BOD of the test and reference substances (e.g. sodium acetate) in simultaneous experimental series. Prepare (at least) two bottles for each determination (blanks, reference and test substances).

a. Dissolve the test substance (amount calculated in step 1) in 157 mL of test medium (measured using the 157 mL overflow measurement flask).

b. If applicable, add 5 drops of nitrification inhibitor (allylthiourea) to the test medium containing the test substance.

c. Add a clean magnetic stirring rod.

d. Add 4 drops of 45% KOH solution to the seal gasket (this will absorb the carbon dioxide). Then insert the seal gasket in the neck of the bottle. The sample must never come into contact with the KOH solution.

e. Place the BOD sensors on the sample bottles and tighten carefully. The system must be completely air-tight.

f. Place the BOD bottles into the bottle rack, and place it in the thermostatically controlled cabinet (e.g. at 20 °C). Connect the stirring system to the electricity.

6) Start the measurement process.

For a measurement period of 1 day, the BOD will be measured hourly.

For a measurement period of 2 days, the BOD will be measured every 2 hours.

For a measurement period of 3-28 days, the BOD will be measured daily.

7) Incubate the sample in accordance with the requirements (e.g. OECD301 for 28 days).

8) Read out stored values. See instructions manual of AL606 biodeg equipment, page 12.

9) Calculate the BOD value for complete biodegradation, according to the exact amount of sample weighed:

$$BOD\ complete\ biodeg\ \left(\frac{mg\ O_2}{L}\right) = mg\ test\ substance * \frac{ThOD \left| mg\ O_2 \right.}{1\ mg\ test\ substance} * \frac{1}{0.157\ L\ water}$$

10) Calculate % biodegradation:

$$\%\ biodegradation = \frac{BOD\ measured\ (\frac{mg\ O_2}{L})}{BOD\ complete\ biodeg\ (\frac{mg\ O_2}{L})} * 100$$

Appendix C

Types of Measurement items from digital microscope

Area

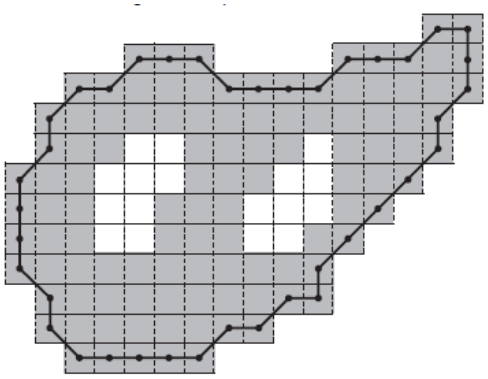
The area of the graphic.

Perimeter

The length of the perimeter of the figure. This is calculated as the length of the line that passes through the center of the pixels that make up the inner perimeter.

Calculation method

This is the perimeter of the specified particle. It is calculated as the length of the line that connects the enters of the pixels along the internal perimeter of the specified particle (the length of the black line in the figure below).



This is calculated while taking the length of the vertical or horizontal line of a pixel as 1, and the length of the diagonal line from a pixel to the diagonally adjacent pixel as $\sqrt{2}$. The value for the figure above is as follows:

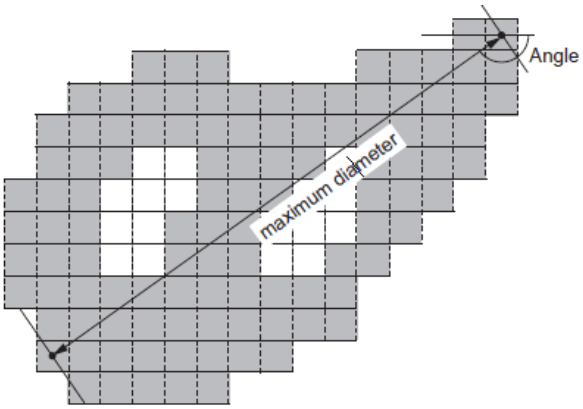
Particle perimeter = 45.2132

When the particle consists of a single pixel, the particle perimeter becomes 0.0.

Maximum diameter

The maximum length between any two points that lie on the inner perimeter of the figure.

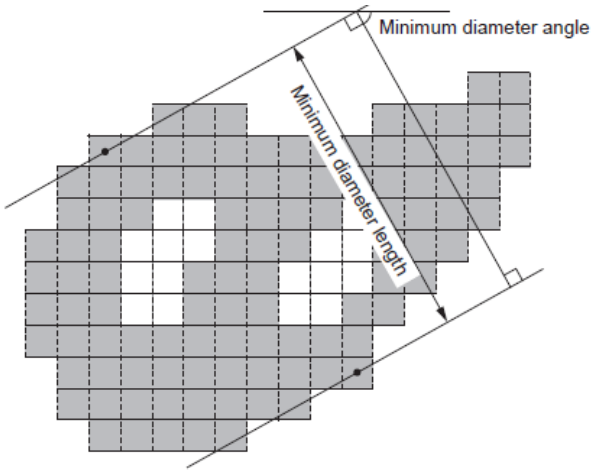
$$= \max_{p,\, q \in C} \sqrt{(px - qx)^2 + (py - qy)^2}$$



The values for the figure above are as follows:
Maximum diameter = 17.204651
Maximum diameter angle = 144.46°

Minimum diameter

This is the minimum possible distance between two parallel lines on either side of the particle. It is calculated as the distance between the pixels that each of the two lines touches.



The values for the figure above are as follows:
Minimum diameter = 10.841152
Minimum diameter angle = 63.4°

Circularity

When the figure is a perfect circle, the maximum value is one. As it becomes long and thin, this value approaches zero.

The degree of circularity of the figure can be shown as: **The degree of circularity of the specified particle =**

$$\frac{4\pi \cdot \text{Area}}{\text{Perimeter}^2}$$

Area is the particle area.

Perimeter is the particle perimeter.

When the particle consists of a single pixel, degree of circularity of the specified particle becomes 1