

Application of the Shrinking Particle Model for the Evaluation of Molecular Recyclability of PET versus Semi-Aromatic Polyesters

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Abstract

The molecular recyclability of poly (ethylene terephthalate) (PET) and three semi-aromatic polyesters poly (phloretic acid) (poly-H), poly (dihydroferulic acid) (poly-G), and poly (dihydrosinapinic acid) (poly-S) is evaluated in this study. PET is an extensively used aromatic polyester, and poly-H, poly-G, and poly-S can be considered semi-aromatic poly (lactic acid) modifications. All these polyesters have been depolymerized at neutral pH and by acid- and base-catalyzed hydrolysis at two temperatures, *i.e.*, 50°C and 80°C. Base-catalyzed depolymerization of virgin PET leads to an isolated yield of 38% after 48 hours of reaction at 80°C. Contrary to these results for PET, almost all the monomers of the semi-aromatic polyesters poly-H, poly-G, and poly-S are recovered with isolated yields larger than 90% at the same temperature after 15 minutes in a facile manner. A shrinking particle model used to determine the global kinetics of the base-catalyzed depolymerization showed that the rate rises with increasing temperature. Using the shrinking particle model, the intrinsic reaction rate constants were determined. It has been demonstrated that the rate coefficients of the depolymerization of the semi-aromatic polyesters poly-H, poly-G, and poly-S are between 2 and 3 orders of magnitude higher than those for PET.

Keywords

Depolymerization, Molecular Recycling, Poly-H, Poly-G, Poly-S, PET, Circular Polymers

1. Introduction

The polyester poly (ethylene terephthalate) (PET) has a well-known application in the packaging industry, e.g., in soft drink bottles. However, PET is primarily used in the textile industry [1] [2]. PET is manufactured from its monomers ethylene glycol (EG) and terephthalic acid (TPA) or dimethyl terephthalate (DMT) by, respectively, an esterification or a transesterification reaction [3] [4]. The major global production of TPA and DMT is intended for the production of PET [5]. The monomers TPA and EG are both derived from petrochemical feedstocks [6]. Because the dependence on oil worldwide has increased tremendously in the last century, the drive to reduce the use of petrochemical feedstocks has grown. Therefore, aiming at recycling PET towards its building blocks (*i.e.*, the monomers) remains essential [7]. Recycling PET and other polymers can be carried out by chemical and thermal/mechanical methods [8]. From a sustainability point of view, (chemical) molecular recycling is the most promising [9] [10], and many chemical procedures suitable to recover the monomers are reported [11].

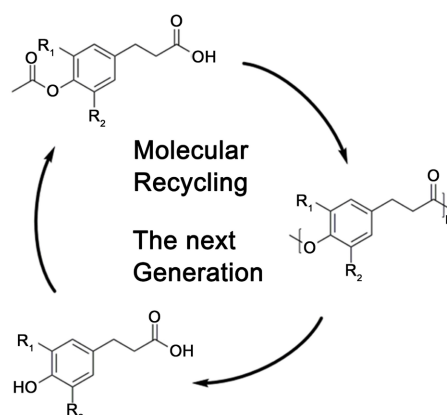
Alternatively, other sources of polyester production could be considered to reduce the required petrochemical feedstock. Lignin is, after cellulose, the most abundant biomass in the world. It has already been demonstrated that it is possible to synthesize semi-aromatic polyesters poly (phloretic acid) (poly-H), poly (dihydroferulic acid) (poly-G), and poly (dihydrosinapinic acid) (poly-S) from ligno-phytochemicals [12]. The semi-aromatic nature of poly-H, poly-G, and poly-S makes them promising candidates for molecular recycling studies [13]. Investigating the molecular recycling pathways of these polyesters can provide insights into designing efficient recycling processes for aliphatic polyesters like PLA, thereby reducing the environmental impact of these materials [14].

Much research has already been performed on the depolymerization of PET. The most applied methods are glycolysis and, to a lesser extent, methanolysis and ammonolysis [15]. Hydrolysis is another method for PET recycling. The main disadvantages of the hydrolysis of PET are the high temperatures (200°C - 250°C), high pressures (1.5 - 2.0 MPa), and the long time needed for complete depolymerization. Hydrolysis of PET is performed at a neutral pH [16] and as acid- and base-catalyzed hydrolysis [17] [18].

This paper reports the results of determining and comparing the global kinetics of PET, poly-H, poly-G, and poly-S hydrolysis reactions. One of the key advantages of semi-aromatic polyesters poly-H, poly-G, poly-S, and PLA is their potential for molecular recyclability through depolymerization and re-polymerization processes. Depolymerization involves breaking down polymer chains into monomers, which can then be purified and used to synthesize new polymer chains. This closed-loop recycling approach offers a sustainable alternative to traditional linear polymer recycling methods and holds promise for reducing the environmental impact of plastic waste, as shown in **Scheme 1**.

Since the hydrolysis of PET in demineralized water and a 1 M sulfuric acid solution did not result in any significant breakdown of PET, only hydrolysis in a

1 M NaOH solution was investigated [19] [20] [21]. After depolymerization, the monomers of all polyesters need to be isolated with high purity (>98%). Such purity levels are necessary to allow re-polymerization with a desired molecular weight build-up and to realize a closed cycle. This paper compares the molecular recycling processes of virgin PET granules (Arnite[®]), PET-flakes of shredded waste bottles, and the three designed homopolyesters: poly-H, poly-G, and poly-S.



Scheme 1. Molecular recycling process for poly (phloretic acid) (poly-H, R₁ = R₂ = H), poly (dihydroferulic acid) (poly-G, R₁ = OCH₃ and R₂ = H), and poly (dihydrosinapinic acid) (poly-S, R₁ = R₂ = OCH₃).

2. Materials and Methods

2.1. Materials

All chemicals (99% purity) were purchased from Sigma-Aldrich and used as received. DMSO-d₆ was purchased from Cambridge Isotope, with 99 at. % deuterated. Virgin PET granules (Arnite[®] A04 900) were purchased from DSM.

2.2. Methods

The depolymerization of polymers was performed in test tubes in an Eppendorf ThermoMixer C with a thermoblock. High-performance liquid chromatography (HPLC) was used to quantify the extent of the depolymerization. The analysis was carried out using a reversed-phase liquid chromatographic system (Agilent 1100 series) equipped with a diode array detector operating at 300 nm (Agilent 1100 series) and an autosampler injector with a 20 μL loop (Agilent 1100 series G1316A). The system had a Grace Alltima C18 5 μm column (250 mm × 4.6 mm). HPLC measurements were made with the following settings: Flow 1.0 mL/min at a temperature of 25 °C, Eluent A = methanol, Eluent B = acetic acid buffer (99% milliQ, 1% acetic acid). The samples were eluted by the following gradient: 40% (v/v) A and 60% (v/v) B as initial conditions and set for 6 min, gradient to 100% A and 0% B in 10 min, 100% A and 0% B set for 5 min. The end conditions 40% A and 60% B are set for 8 min.

2.3. Depolymerization Procedures

Procedure for the depolymerization of PET in 1M NaOH applied:

To measure hydrolytic degradation, virgin PET granules (Arnite[®]) and shredded PET waste bottles were finely ground (particles smaller than 180 μm). These PET particles were distributed over 8 test tubes in equal amounts of 20 mg. 1.0 mL of 1 M NaOH solution was added and incubated at three temperatures (25°C, 50°C, and 80°C \pm 1°C) with agitation at 500 rpm using a controlled environment incubator shaker. At different time intervals (1, 2, 4, 8, 16, 24, and 48 hours after the start of the reaction), the content of a specific test tube was neutralized with 1.0 mL of 1 M H₂SO₄. 2.0 mL of methanol and 0.4% v/v toluene as internal standard was added and the content of the test tube was analyzed by high-performance liquid chromatography (HPLC). So, for every depolymerization experiment, there were 8 samples for conversion measurement, *i.e.*, one test tube gives one conversion. All samples were filtered using 0.45 μm PTFE syringe filters and injected (20 μL) using an autosampler. Absorbance was monitored at $\lambda = 254$ nm, and concentrations were calculated from a calibration curve of known terephthalic acid standard solutions relative to toluene as an internal standard.

In addition, 1.0 g PET was hydrolyzed for 48 hours after the start of the reaction at a temperature of 80°C \pm 1°C. After hydrolysis, the reaction mixture was filtered to separate the unreacted polymer from the monomers in the solution. The unreacted polymer was dried in a vacuum oven at 50°C for 24 hours and used to confirm the total mass balance. The remaining solution contains disodium terephthalate (TPA-Na) and ethylene glycol (EG). To end up with the monomer terephthalic acid (TPA) instead of its disodium salt, the solution was acidified to a pH of 3 with a 1 M aqueous sulfuric acid solution. TPA precipitated and was separated by filtration. After drying, the isolated yield of the monomer TPA was 38% (with a selectivity of 95% towards TPA verified by HPLC) for the hydrolysis reaction of virgin PET at 80°C.

Procedure for the depolymerization of poly-H in 1M NaOH applied:

To measure hydrolytic degradation, poly-H was finely ground (particles smaller than 180 μm) and was distributed over 8 test tubes with equal amounts of 20 mg poly-H to which 1.0 mL of 1 M NaOH solution had been added and incubated at 80°C with agitation at 500 rpm using a controlled environment incubator shaker. At different time intervals, the content of a specific test tube was neutralized with 1.0 mL of 1 M H₂SO₄. 2.0 mL of methanol and 0.4% v/v toluene as internal standard was added. The content of the test tube was analyzed by HPLC. So, for every depolymerization experiment, there were 8 samples for conversion measurement: one test tube gives one conversion. All samples were filtered using 0.45 μm PTFE syringe filters and injected (20 μL) using an autosampler. Absorbance was monitored at $\lambda = 254$ nm, and concentrations were calculated from a calibration curve of known dihydrocoumaric acid standard solutions relative to toluene as an internal standard.

Procedure for the depolymerization of poly-H in 1M H₂SO₄ applied:

The release of dihydrocoumaric acid from polymer poly-H was evaluated by molecular recycling in 1 M H₂SO₄. To measure hydrolytic degradation, poly-H was finely ground (particles smaller than 180 μm) and was distributed over 8 test tubes with equal amounts of 20 mg poly-H to which 1.0 mL of 1 M H₂SO₄ had been added and incubated at 80 °C with agitation at 500 rpm using a controlled environment incubator shaker. At different time intervals, 2.0 mL of methanol and 0.4% v/v toluene as internal standard was added to the content of a specific test tube and analyzed by HPLC. So, for every depolymerization experiment, there were eight samples for conversion measurement: one test tube gives one conversion. All samples were filtered using 0.45 μm PTFE syringe filters and injected (20 μL) using an autosampler. Absorbance was monitored at $\lambda = 254$ nm, and concentrations were calculated from a calibration curve of known dihydrocoumaric acid standard solutions and 0.4% v/v toluene as an internal standard.

3. Results and Discussion

Previously, a green, efficient, and scalable method was developed to produce cinnamic acid analogs from 4-hydroxybenzaldehyde by condensation with malonic acid [22] [23]. This Knoevenagel reaction and subsequent hydrogenation generated polymerizable 4-hydroxy-dihydro cinnamic acid monomers. Earlier, we described how these monomers are polymerized into semi-aromatic molecularly recyclable polyesters poly-H, poly-G, and poly-S [24] [25]. These semi-aromatic polyesters typically have alternating aromatic units but aliphatic ester groups in their backbone. Because the aliphatic ester bonds are decisive in the degradability of PLA, these semi-aromatic polyesters, poly-H, poly-G, and poly-S, are suitable models for studying the hydrolysis of aliphatic polyesters. In this sequel paper, the results of the depolymerization of the semi-aromatic molecularly recyclable polyesters poly-H, poly-G, and poly-S are compared with the results of the depolymerization of virgin PET granules (Arnite[®]) and shredded PET waste bottles.

First, a mathematical model was developed to describe the kinetics of depolymerization. It should be pointed out that the derivation of a comprehensive mathematical model is rather complicated since mass-transfer phenomena (between the solid and the liquid phase) occur in series with the hydrolysis reaction [26].

The model assumes that all depolymerization reactions occur at the surface of a non-porous (highly crystalline) solid particle. Over time, the solid particle will shrink as the polymer is depolymerized into its monomer(s), whereby the monomers migrate to the bulk liquid phase by mass transfer. The shrinking particle model (also known as the shrinking core model) has been developed to get insight into the global kinetics of depolymerization [25]. For the reactions with no product layers formed outside the unreacted core, *i.e.*, when products are either dissolved in the surrounding fluid or removed immediately from the outer surface of the solid, the shrinking core model is also called shrinking particle model

[26]. The polymer particles are assumed to be spherical and have the same diameter, equal to the weighted average diameter of the particle size class. The depolymerization of the polymer is relatively slow (*i.e.*, the time constant for reaction \gg time constant for mass transfer), so the overall hydrolysis process is reaction controlled. Furthermore, the solid particles are ideally mixed with the liquid phase, and the catalyst (acid or base) concentration (C_c [mol/m³]) at the locus of reaction remains constant during the reaction and is equal to the bulk concentration. The depolymerization reaction is assumed to be first-order in the polymer concentration (which is represented by the surface area (S_p [m²]) of the polymer particle), and first-order in the acid or base concentration (sodium hydroxide or sulfuric acid). The reaction volume remains constant during hydrolysis, and no reversible reaction (*i.e.*, ester formation) occurs.

The molar balance (Equation (1)) describes the depolymerization for one particle:

$$\frac{dN_p}{dt} = -k_r S_p C_c \quad (1),$$

where N_p [mol] is the number of moles of the polymer repeating units in one particle and k_r [m³/(m²·s)] is the reaction rate constant of depolymerization at the surface of the particle.

N_p can be expressed in terms of C_p , the number of moles repeat units present per unit volume of the particle (*i.e.*, the ratio of the density of the polymer particle (kg/m³), the molecular mass of the repeat unit (kg/mol) and the volume of the particle V_p thus $N_p = C_p \cdot V_p$, and Equation (1) becomes,

$$\frac{d(C_p V_p)}{dt} = -k_r S_p C_c \quad (2),$$

Expressing V_p and S_p in terms of d_p , the diameter of the spherical particle, and substituting in Equation (2) results in:

$$\frac{d(d_p)}{dt} = -\frac{2k_r C_c}{C_p} \quad (3),$$

Then, the conversion of the polymer can be described as:

$$X = 1 - \frac{V_p}{V_{p,0}} = 1 - \frac{d_p^3}{d_{p,0}^3} \quad (4),$$

$$d_p = (1 - X)^{1/3} d_{p,0} \quad (5).$$

Substitution of Equation (5) into Equation (3) leads after rearrangement to Equation (6):

$$\frac{d(1 - X)}{dt} = -\frac{2k_r C_c}{C_p d_{p,0}} (1 - X)^{2/3} \quad (6).$$

Integration gives:

$$(1 - X)^{1/3} - 1 = -k_{obs} t \quad (7),$$

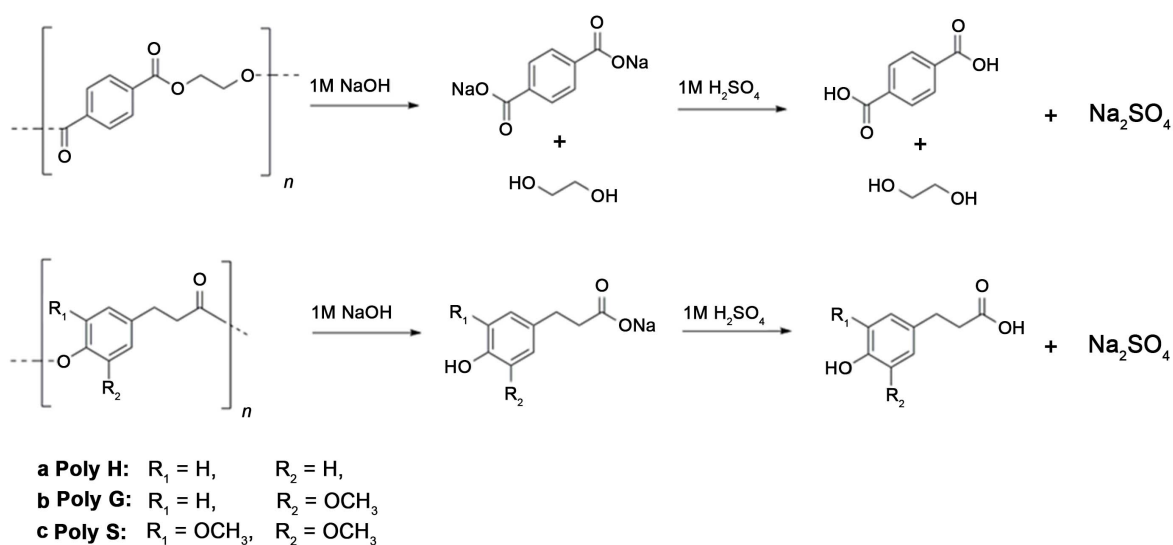
where:

$$k_{obs} = \frac{2k_r C_C}{3C_p d_{p,0}} [1/s].$$

When depolymerization occurs at the surface of the solid polymer particle, the particle size is important since it determines the effective surface area per unit reaction volume. In all further experiments, only the fraction with particle sizes $\leq 180 \mu\text{m}$ has been used to explore the depolymerization rates.

The hydrolysis of virgin PET granules and shredded PET waste bottles in demineralized water at room temperature did not result in any breakdown of PET. Nevertheless, it is possible to depolymerize PET by neutral or acid hydrolysis, but much higher temperatures and pressures are required [27] [28] [29].

As with PET, the hydrolysis of poly-H, poly-G, and poly-S in demineralized water did not break the polymer after 48 hours of reaction time at 25 °C, 50 °C, or 80 °C. A comparison of the semi-aromatic polyesters with PET polyesters was done using base-catalyzed hydrolysis. Base-catalyzed hydrolysis of PET is usually carried out in an aqueous NaOH solution with a concentration of 4 - 20 wt% [5] [30] [31]. The reaction products are ethylene glycol and disodium terephthalate. After neutralization with H_2SO_4 to a pH of 3, terephthalic acid is recovered with ethylene glycol and sodium sulfate, as presented in **Scheme 2**.



Scheme 2. Base-catalyzed hydrolysis of PET and the semi-aromatic polyesters (poly-H, poly-G, and poly-S). The reaction products of PET are ethylene glycol, and the disodium terephthalate salt, and the reaction products of poly-H, poly-G, and poly-S are the di-hydrocinnamic carboxylates.

The results of the base-catalyzed hydrolysis of PET and molecularly recyclable polyesters poly-H, poly-G, and poly-S are presented in **Figure 1**. After 48 hours of reaction, the conversion reached for PET waste particles was 50% at a temperature of 80 °C. Note that the conversion of virgin PET particles is significantly lower for the same reaction time. This faster conversion of shredded PET waste bottles can be attributed to the material being mainly amorphous, contrary to virgin PET, which is more crystalline. Also, additives like isophthalic acid and

2-methyl-1,3-propanediol used to enhance the amorphous state of shredded PET bottles may influence the depolymerization rate [32] [33] [34]. Note that, in **Figure 1**, the timescale for the depolymerization of the semi-aromatic polyesters is in minutes, whereas the depolymerization of PET is shown in hours. At 80 °C, all three semi-aromatic polyesters are almost entirely converted into monomers in about 15 minutes.

Figure 1 also shows that temperature influences the depolymerization rate. A higher temperature leads to a considerable increase in the reaction rates in all polyesters examined, which reveals that the resistance against reaction is much larger than the resistance of mass transfer of NaOH to the reaction products for the reactive surface.

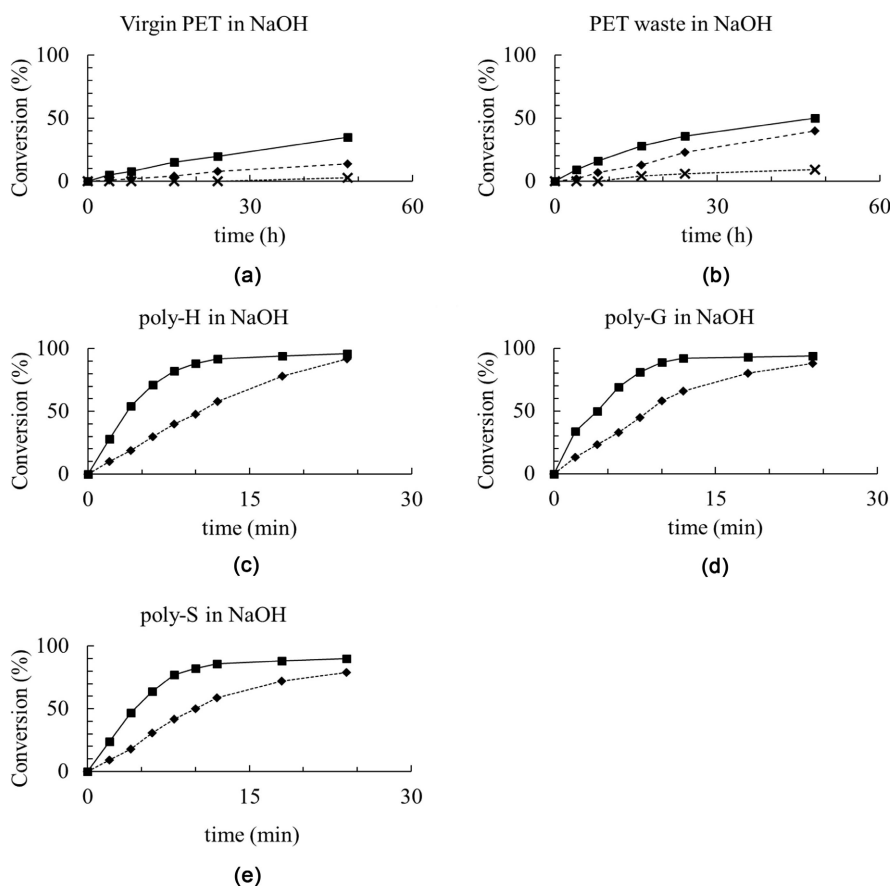


Figure 1. Conversion time history of the depolymerization of virgin PET (a), PET waste particles (b), poly-H (c), poly-G (d), and poly-S (e) in a 1 M aqueous sodium hydroxide solution at 25 °C (x); 50 °C (♦) and 80 °C (■), $d_{p,0} \leq 180 \mu\text{m}$, solid content: 5% w/w. Reported conversions are based on a calibration curve of the monomer with toluene as an internal standard at 254 nm.

The mathematical model developed has been applied to the experimental data. Because at 25 °C hardly any conversion has been observed for PET, this temperature has not been taken into account. In **Figure 2** the observed values of $\left[1 - (1 - X)^{1/3}\right]$ have been plotted against time (t). According to Equation (8)

the slope of the linear relation between $[1-(1-X)^{1/3}]$ and t is equal to k_{obs} . The rate coefficient k_r has been calculated from k_{obs} by Equation (9). Note that the concentration of repeat units (C_p) for PET is equal to the ratio of the density of PET (1370 kg/m_s^3) [35] [36] and the molecular weight of the repeat unit (0.1922 kg/mol), so C_p for PET is 7130 mol/m_s^3 .

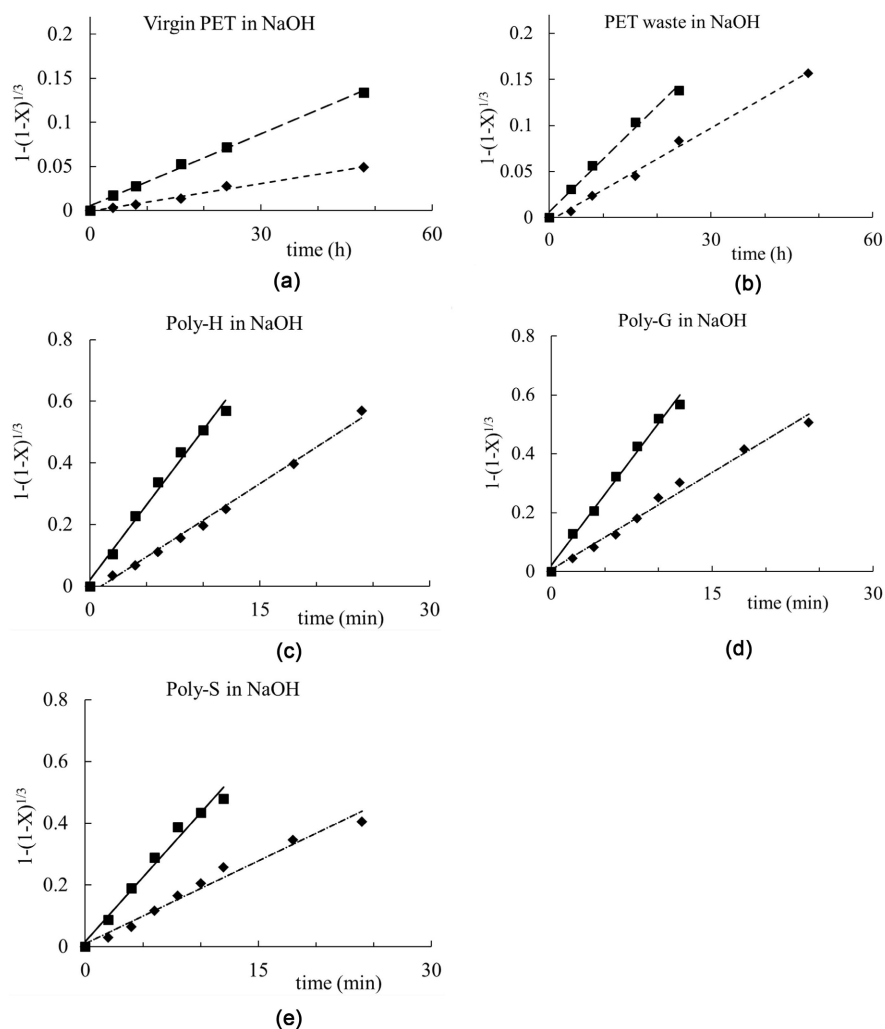


Figure 2. Evaluation of the kinetics of alkaline catalyzed depolymerization of virgin PET (a), PET waste particles (b), poly-H (c), poly-G (d), and poly-S (e) according to Equation (8). \blacklozenge : 50°C, and \blacksquare : 80°C, $d_{p,0} \leq 180 \mu\text{m}$.

Assuming the same density for the semi-aromatic polyesters as for PET and using the molecular weights of the repeat units 0.148, 0.178, and 0.208 kg/mol for poly-H, poly-G, and poly-S, respectively, the C_p -values for poly-H, poly-G and poly-S are 9257, 7697 and 6587 mol/m_s^3 , correspondingly. For the catalyst concentration and initial particle size, the following values have been used in Equation (9): $C_c = 1000 \text{ mol/m}_s^3$ and $d_{p,0} = 180 \mu\text{m}$. **Table 1** presents the reaction rate constants k_{obs} and k_r at 50°C and 80°C, including their correlation coefficient ($R^2 > 0.99$), and the rate k_{obs} relative to that of virgin PET (Arnite[®]).

Given the experimental results, the reaction times for complete depolymerization of semi-aromatic polyesters poly-H, poly-G, and poly-S are much shorter than those for PET. Compared to the reaction rate constants of PET, the rate constants (k_r) for depolymerization of poly-H, poly-G, and poly-S are between two and three orders of magnitude larger than those for PET. However, it must be pointed out that the chain length and the crystallinity of the polymer may have a considerable influence on the depolymerization rate.

Table 1. Reaction rate constants k_{obs} and k_r for the base-catalyzed depolymerization of virgin PET, PET waste particles, poly-H, poly-G, and poly-S at 50°C and 80°C.

	k_{obs} (323K) s ⁻¹	R ²	k_r (323 K) m ₁ ³ · m _s ⁻² · s ⁻¹	rate relative to Arnite®	k_{obs} (353K) s ⁻¹	R ²	k_r (353 K) m ₁ ³ · m _s ⁻² · s ⁻¹	rate relative to Arnite®
Virgin PET Arnite®	292 × 10 ⁻⁹	0.990	562 × 10 ⁻¹²	1	758 × 10 ⁻⁹	0.996	1.46 × 10 ⁻⁹	1
PET waste	931 × 10 ⁻⁹	0.994	1.79 × 10 ⁻⁹	3	1592 × 10 ⁻⁹	0.989	3.06 × 10 ⁻⁹	2
poly-H	395 × 10 ⁻⁹	0.993	988 × 10 ⁻⁹	1758	810 × 10 ⁻⁶	0.987	2.02 × 10 ⁻⁶	3602
poly-G	367 × 10 ⁻⁹	0.991	763 × 10 ⁻⁹	1357	806 × 10 ⁻⁶	0.988	1.67 × 10 ⁻⁶	2982
poly-S	298 × 10 ⁻⁹	0.978	531 × 10 ⁻⁹	944	695 × 10 ⁻⁶	0.981	1.24 × 10 ⁻⁶	2200

k_r calculated from k_{obs} using Equation (9) with $C_p = 7130, 9257, 7697$ and 6587 mol/m_s³ for PET, poly-H, poly-G, and poly-S. $C_c = 1000$ mol/m_l³ and $d_{p0} = 180 \times 10^{-6}$ m.

After hydrolysis, the monomers have to be separated from the solvent. First, the unreacted PET was separated by filtration. The remaining solution contains disodium terephthalate (TPA-Na) and ethylene glycol (EG). To end up with terephthalic acid (TPA), the solution was acidified to a pH of 3 with a 1 M aqueous sulfuric acid solution instead of its disodium salt. TPA precipitated and was separated by filtration. After drying, the isolated yield of the monomer TPA was 38% for the hydrolysis reaction of virgin PET at 80°C. The filtrate contains ethylene glycol (EG), water, and dissolved salt (Na₂SO₄). Separation of ethylene glycol involves the removal of the salt. Ethylene glycol (boiling point = 197.3°C) and water can be easily separated by distillation. However, the salt remains in the EG fraction and moderately precipitates. In this research, the salt was removed by filtration, which led to an isolated yield of 28% of EG. Some improvement in this separation technique is required.

Previously, the recovery of the poly-H, poly-G, and poly-S monomers was described with the acidifying step in a comparable way to the recovery of the monomers of PET [24] [25]. Because the monomers of the semi-aromatic polyesters are moderately soluble in water, extraction was a proper separation technique. Toluene, ethyl acetate, methyl-*tert*-butyl-ether (MTBE), n-heptane, and n-pentane were tested as solvents. Toluene, n-heptane, and n-pentane are not suitable because the monomers of the semi-aromatic polyesters are not soluble in any of these solvents. Dihydrocoumaric acid dissolves in ethyl acetate and

MTBE. The partition coefficient for the system ethyl acetate/water was determined to be approximately 40 $\left[\frac{dm^3_{\text{water}}}{dm^3_{\text{ethyl acetate}}} \right]$.

However, it must be pointed out that ethyl acetate and MTBE are also slightly soluble in water, so a ternary phase diagram is required for an accurate design of the extraction process. A ternary phase diagram has not been taken into account in this study. Also, there is no knowledge yet about the activities of dihydrocoumaric acid in water, ethyl acetate, or MTBE. So, further thermodynamic research on separating the monomers of the semi-aromatic polyesters is required.

Acid hydrolysis of PET is performed frequently using concentrated sulfuric acid, although other mineral acids like nitric or phosphoric acid have also been used [37]. A substantial drawback of PET hydrolysis in concentrated sulfuric acid is the corrosive solid nature of the reaction system and the generation of aqueous waste. The hydrolysis of PET in 1 M sulfuric acid did not show any breakdown after 48 hours. The acid-catalyzed hydrolysis in a 1 M sulfuric acid solution of poly-H, poly-G, and poly-S looks promising, as shown in **Figure 3**. Note that base-catalyzed depolymerization does not solve the problem of producing salt during workup. So, it is recommended that the depolymerization of the semi-aromatic polyesters with acid-catalyzed hydrolysis be investigated.

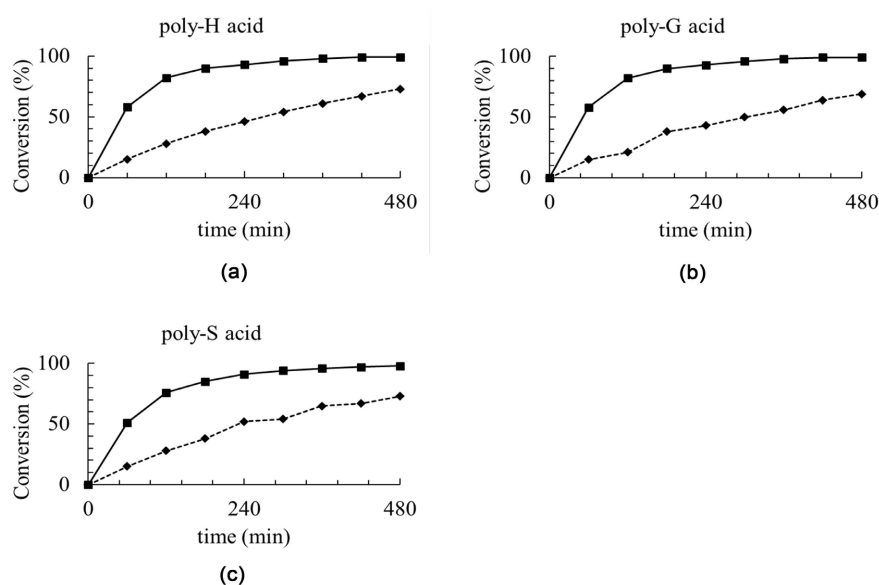


Figure 3. Conversion time history of the depolymerization of poly-H (a), poly-G (b), and poly-S (c) in a 1 M aqueous sulfuric acid solution at 50°C (♦) and 80°C (■), $d_{p,0} \leq 180$ μm , solid content = 5% w/w. Reported conversions are based on a calibration curve of the monomer with toluene as an internal standard at 254 nm.

4. Conclusions

The molecular recyclability of fully aromatic polyester PET and the semi-aromatic polyesters poly-H, poly-G, and poly-S has been examined. It was found that the hydrolysis of virgin PET granules and shredded PET waste bottles, as

well as the semi-aromatic polyesters poly-H, poly-G, and poly-S in demineralized water, did not noticeably occur after 48 hours of reaction time at 25 °C, 50 °C, and 80 °C.

Base-catalyzed depolymerization of virgin PET leads to a low conversion after 48 hours of reaction at 80 °C. The monomer terephthalic acid can easily be isolated by acidification and precipitation, leading to an isolated yield of 38% TPA. The base-catalyzed depolymerization of the semi-aromatic polyesters poly-H, poly-G, and poly-S is fast and in highly isolated yields (>90%). A shrinking particle model, used to value the intrinsic reaction rate constants, demonstrated that the rate coefficients of the depolymerization of the semi-aromatic polyesters poly-H, poly-G, and poly-S are 3 orders of magnitude larger than those for the fully-aromatic ester PET. Comparable rate coefficients are expected for PLA with comparable aliphatic ester groups.

PET hydrolysis in 1 M aqueous sulfuric acid is very slow, and no depolymerization was observed after 48 hours of reaction. The semi-aromatic polyesters poly-H, poly-G, and poly-S were depolymerized entirely in a 1 M sulfuric acid solution after 4 hours at 80 °C. The advantage of acidic depolymerization is that no extra step of acidification is required after depolymerization, and there is no additional salt formation.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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