

Synthesis of Polyesters from Azelaic Acid and Glycerol by Polycondensation Reaction

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Abstract

Thermal polycondensation was used to synthesize bio-based polyester poly(glycerol azelate) (PGAz) from glycerol and azelaic acid. Under the condition of 1.0:1.0 molar ratio of azelaic acid to glycerol at 140 °C for 24 h, the highest number- and weight-average molecular weights of 1502 and 8653 g/mol were obtained with the 92.22 % of acid conversion and 78.13 % of the polyester yield. Based on NMR analysis, the structure of PGAz was found as a network polyester with linear and dendritic substitution patterns of azelaic acid on the glycerol units via ester bonds. Moreover, the differential scanning calorimeter and thermal gravimetric analysis were also used to investigate the glass transition temperature and thermal stability of synthetic PGAz.

Keywords: biopolymer, polyester, glycerol, polycondensation

Introduction

Biodegradable polymers had been developed as an alternative way to solve the problems of environmental pollution and waste management from bio-resistant synthetic plastics [1]. Many countries put forth attention on synthesis of biodegradable polymers because of the applications in many fields such as packaging, paper coating, agriculture, sanitary, fibers, film and biomedical applications. Moreover, the hydrolytic and enzymatic degradation residue of these polymers are normally non-toxic and naturally metabolized [2,3].

Several arguments believe in the great potential of plant oils as an alternative resource for the

polymer production because of their world-wide availability, non-toxicity, relatively low prices and renewability. The main components of plant oils are triglycerides which are the ester products from one molecule of glycerol and three molecules of fatty acids [4]. Triglycerides are compounded with several active chemical sites (double bonds and ester groups) that can be used for the cross-linked polymer synthesis [5,6]. On the other hand, the hydrolysis of triglycerides provides glycerol and a mixture of fatty acids. Glycerol is widely used as building block in polymer production and fatty acids have been used directly or modify to perform the suitable monomers for polymeric productions.

In recent years, there are many researches of biodegradable polymer with various types such as polyester, polyurethane, polyamide, polyesteramide and polynaphthol [7]. However, polyester has been of great interest because of their susceptibility to biological attacks. Polyesters can be synthesized from polycondensation reaction of glycerol and fatty acids. In this study, the monomers of choice are azelaic acid and glycerol. Azelaic acid is a diacid that was derived from oxidation by oleic acid in palm oil [8] and glycerol can be obtained as a byproduct from biodiesel production. Therefore, the use of two monomers should give the value added process of plant oil and production of thermoset polyester which has a good flexibility, biocompatibility and biodegradation [9].

The obtained polyester of poly(glycerol azelate) (PGAz) from polycondensation were identified the structure by fourier transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance spectroscopy (¹H-NMR) and carbon nuclear magnetic resonance spectroscopy (¹³C-NMR). The effect of reaction temperature on the average molecular weights and distribution of the polyester was investigated by size exclusion chromatography (SEC) to obtain the optimized condition of the synthesis of PGAz. Moreover, polyester was also analyzed by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) for their thermal properties and thermal stability.

Materials and Methods

Materials

Azelaic acid and deuterated chloroform (*d*-CDCl₃) were purchased from Sigma-Aldrich. Glycerol was purchased from QR&C. Tetrahydrofuran (THF) was purchased from J.T.Baker. All chemicals were used as received without any further purification.

Synthesis of polyester

The bulk reaction was performed in a batch reactor. Azelaic acid and glycerol were mixed in a two-necked flask with a molar ratio of 1.0:1.0. The mixture was heated until azelaic acid was completely melted about 0.5 h in a reflux apparatus. The mixture was purged with nitrogen and heated at 120, 130 or 140 °C for 24 h under atmospheric pressure. The polyesters were characterized and analyzed without purification.

Characterization of polyester

FTIR spectra of the resulting polyester and remained monomers were recorded by a PerkinElmer spectrum one Transform Infrared Spectroscopy. ¹H- and ¹³C-NMR spectra of polyester solution in deuterated chloroform (*d*-CDCl₃) were recorded on a Bruker at 400 MHz. Tetramethylsilane was used as the internal reference standard.

SEC was performed on a Shimadzu, LC-10A dvp at 40 °C. THF was used as mobile phase at a flow rate of 1 ml/min with a polystyrene solution in THF as a calibration standard. The number average molecular weight (\bar{M}_n), weight average molecular weight (\bar{M}_w) and polydispersity index (PDI) were calculated using a calibration curve.

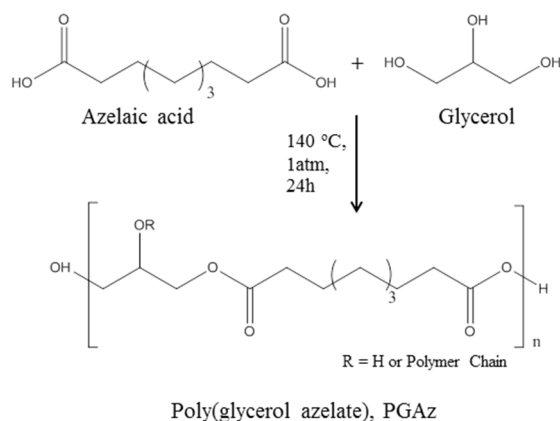
DSC was recorded using METTLER TOLEDO 822e. The samples (10 mg) were placed in an aluminium pan, heated from -100 to 150 °C under a nitrogen flow rate of 20 ml/min and the heating rate of 10 °C/min to obtain the the glass transition temperature (T_g).

Thermal gravimetric experiments of the polyester samples were conducted on a PerkinElmer, Pyris Diamond TG/DTA. The samples (10 mg) were placed in a platinum pan and heated up to 1000 °C from room temperature at a rate of 10 °C/min. Nitrogen was used as purge gas at a flow rate of 50 mL/min.

Results and Discussion

Synthesis of PGAz polyester

The synthesis of PGAz was performed through bulk polycondensation reaction of azelaic acid and glycerol monomers as shown in Scheme 1. The effect of reaction temperature to \overline{M}_n , \overline{M}_w and distribution of PGAz was studied under the molar ratio of azelaic acid to glycerol of 1.0:1.0 for 24 h. Table 1 summarizes the acid conversion, yield and average molecular weights of PGAz at various reaction temperatures, i.e., 120, 130 and 140 °C. It was found that \overline{M}_n , \overline{M}_w and PDI of PGAz tended to be increased with the increase of reaction temperature, resulted from the increase of reaction rate by the disproportionately increase in the number of high energy collisions. However, since the polymer discoloration occurred at ≥ 150 °C [10], the experiment was not carried out at higher temperature. Additionally, by increasing molecular weights of polymer the formation of gels occurred, leading to the difficulty of solubility in solvent and processing. The broad distribution of molecular weight according to the high PDI value indicated that more random dispersion occurred instead of mono dispersion in polyester structures. The condition that gave the highest average molecular weights was at reaction temperature of 140 °C with the 92.22 and 78.13 % of acid conversion and yield of PGAz, respectively.



Scheme 1. Synthesis of poly(glycerol azelate) polymer.

Characterization of PGAz polyester

The resulting PGAz was then characterized by FTIR, ¹H-NMR and ¹³C-NMR spectroscopy to indicate the functional groups and structure. Figure 1 shows the FTIR spectra of glycerol, azelaic acid and the resulting PGAz carried out at 120, 130 and 140 °C. The adsorption peaks of glycerol at 923 and 3368 cm⁻¹ were assigned to O-H bending and O-H stretching of hydrogen-bonded hydroxyl groups and a peak at 1040 cm⁻¹ corresponded to C-C-O stretching (Fig. 1(a)) [2,11]. The adsorption peaks at 927, 1252 and 1698 cm⁻¹ belonged to O-H bending, C-C=O-O stretching and carbonyl (C=O) group stretching of the carboxyl groups (-COOH) of azelaic acid (Fig. 1(b)) [2,11]. Figures 1(c) – 1(e) show the spectra of

Table 1: Acid Conversion, yield and average molecular weights of poly(glycerol azelate) at various reaction temperatures.

Reaction temperature (°C)	Acid conversion (%)	Yield (%)	\overline{M}_n^a (g/mol)	\overline{M}_w^a (g/mol)	PDI ^a ($\overline{M}_w/\overline{M}_n$)
120	83.12	63.95	434	1072	2.47
130	88.89	74.07	795	2461	3.09
140	92.22	78.13	1502	8653	5.76

^a Data from SEC were measured using THF as solvent.

Condition: 1.0:1.0 molar ratio of azelaic acid to glycerol for 24 h.

the PGAs synthesized at 120 °C to 140 °C, respectively, that have similar pattern. The adsorptions of the ether (C-O) group stretching and carbonyl (C=O) group stretching of the ester group were observed at 1176-1181 and 1733-1735 cm⁻¹, respectively. Additionally, it is clearly observed the reduction of adsorption peaks of carbonyl group stretching of acid ($\delta = 1698$ cm⁻¹), O-H bending ($\delta = 923$ cm⁻¹) and O-H stretching ($\delta = 3368$ cm⁻¹) of hydroxyl groups of glycerol [2,6,11]. The peaks of C-H bending and C-H stretching of the methylene groups appeared at 1457-1458 and 2933-2934 cm⁻¹. The peak at 2858-2859 cm⁻¹ corresponded to the C-H stretching of methyl groups of PGAs [6].

Figure 2(a) shows a ¹H-NMR spectrum of PGA prepared from the polycondensation at 140 °C. The singlet peak of central methylene group of azelaic acid (AA 4-6) was observed at 1.32 ppm. The methylene group at β position of carbonyl group of azelaic acid (AA 3,7) was observed as the quartet peak at 1.61 ppm and the methylene group at α position of carbonyl group of azelaic acid (AA 2,8) was observed as the multiplet peak at 2.33 ppm. The methylene (G 1,3) and methane (G 2) of the glycerol unit were observed at 3.45-4.50 and 4.80-5.45 ppm, respectively [6,12]. As shown in Figure 2(b), a ¹³C-NMR spectrum of PGA shows the peaks of methylene and methane groups of the glycerol unit (G 1-3) at 68.2-72.1 ppm. The peaks at 28.5-29.7 ppm corresponded to the central methylene group of the azelaic acid unit (AA 4-6). The peaks for the methylene groups of the azelaic acid unit at β position (AA 3,7) and α position (AA 2,8) of the carbonyl group appeared at 24.5-24.7 and 33.8-34.2 ppm, respectively. The peaks at 173.9 and 178.7 ppm was assigned to the carbonyl groups of the azelaic acid unit linkage with glycerol and the free azelaic acid unit (AA 1,9) [6].

¹³C-NMR was also used to investigate the substitution patterns of the glycerol units in the polyester chains. Figure 3 shows the ¹³C-NMR spectrum of PGA in the ranges of 68-73 and 173-180 ppm. The different substitution patterns of glycerol units in the polymeric chains and their corresponding methine (-CH-) with linkage diacid subunits by carbonyl ester group were founded in 4 patterns of terminal units ($\delta = 70.3$ ppm), linear units on 1,2-positions of the glycerol unit (L_{1,2}) ($\delta = 68.2$ ppm), linear units on 1,3-positions of the glycerol unit (L_{1,3}) ($\delta = 72.1$ ppm) and dendritic units ($\delta = 68.2$ ppm) [10]. Figure 3(b) shows the patterns of azelaic acid subunits which founded as the azelaic units esterified with glycerol unit at 174.0 ppm and be as free acid terminal units at 179.2 ppm [10]. Accordingly, the structure of PGA was found as a network polyester with linear and dendritic substitution patterns of azelaic acid on the glycerol units via ester bonds.

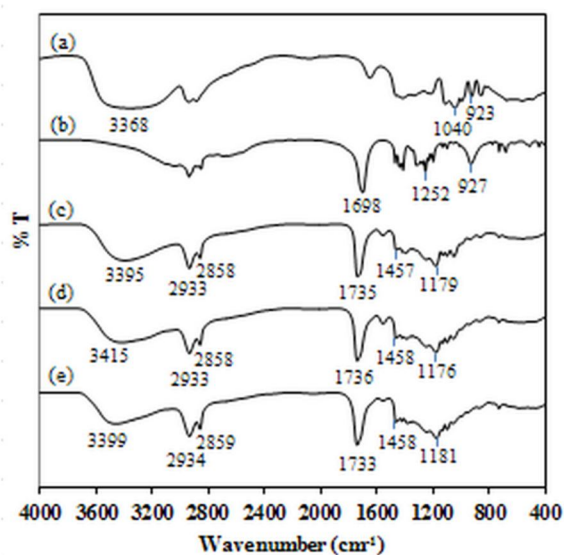


Figure 1. FT-IR spectra of (a) glycerol, (b) azelaic acid, PGA prepared at (c) 120 °C, (d) 130 °C and (e) 140 °C.

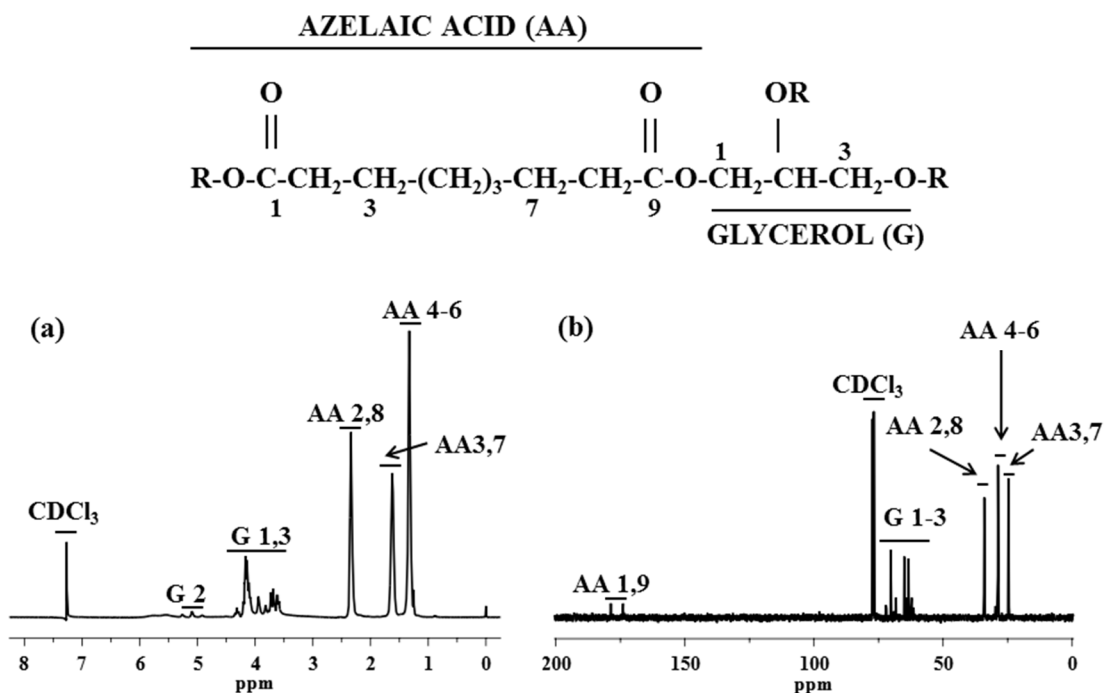


Figure 2. (a) ¹H-NMR spectra and (b) ¹³C-NMR spectra of PGaz obtained from the polycondensation at 140 °C.

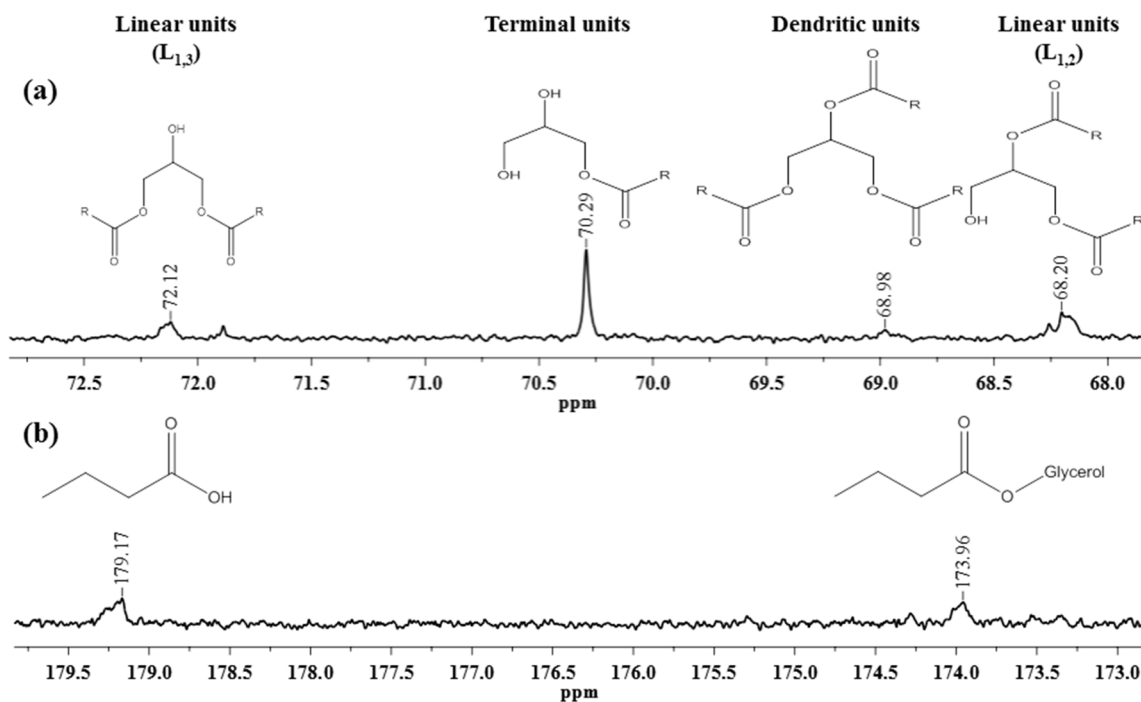


Figure 3. ¹³C-NMR spectra of PGaz obtained from the polycondensation at 140 °C in the range between (a) 68 and 73 ppm and (b) 173 and 180 ppm.

Thermal properties of PGAz

From DSC thermatogram (Figure 4(a)) reveals that T_g value of PGAz synthesized at 140 °C was detected at -41 °C. Figure 4(b) shows the weight loss by thermal decomposition of PGAz synthesized at 140 °C. The 10 % of the beginning mass loss was used to define the thermal stability of PGAz which obtained below 250 °C. Finally, the degradation of PGAz was totally lost at the temperature of 476 °C.

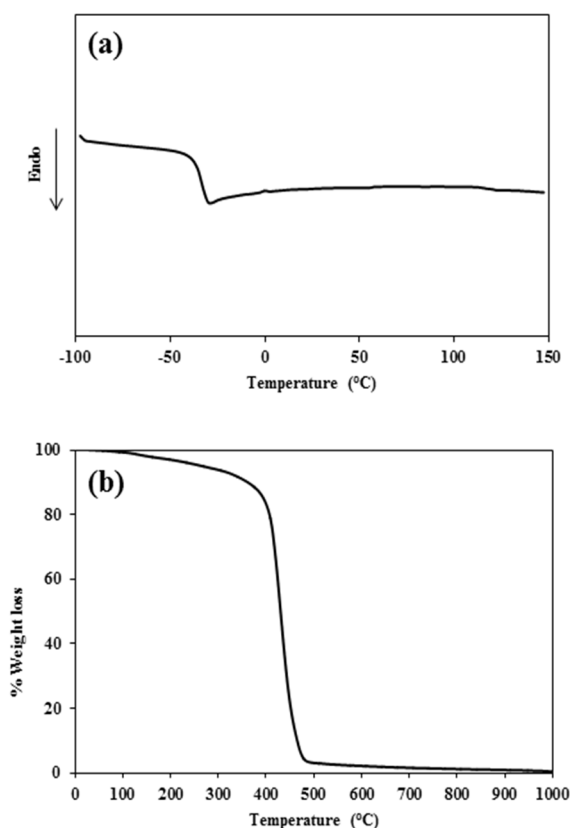


Figure 4. (a) DSC and (b) TGA thermograms of PGAz.

Conclusions

Poly(glycerol azelate) (PGAz) was synthesized from azelaic acid and glycerol by thermal polycondensation reaction. Under a condition using a azelaic acid:glycerol molar ratio of 1.0:1.0 and a reaction time of 24 h, the acid conversion, yield and average molecular weights were found to be highest

when the reaction temperature of 140 °C was used. According to the structure analysis by NMR spectra, the substitution patterns of the glycerol units were found to be linear and dendritic units with the coexistence of the hydroxyl and free acid terminal units. The resulting PGAz exhibited T_g of -41 °C and thermal stability below 250 °C.

Acknowledgments

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