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SYNTHESIS AND ENZYMATIC DEGRADATION OF ALIPHATIC POLYESTERS COPOLYMERIZED WITH TRIMESIC ACID

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ABSTRACT

Network copolyesters were made from adipic acid and ethylene glycol with 10–40 mol% trimesic acid (Y). Prepolymers prepared by melt polycondensation were cast from dimethylformamide solution and postpolymerized at 260°C for various times to form a network. The degree of reaction (D_R), estimated from the infrared absorbance of hydroxyl and methylene groups, increased with increasing postpolymerization time and leveled out at about 90% after 4–6 hours. Heat distortion temperatures (T_h) measured by thermomechanical analysis increased greatly from −83 to 48°C upon the incorporation of Y. Wide-angle x-ray diffraction patterns showed that the copolymer films are amorphous. Density, tensile strength, and Young's modulus decreased for the copolymers with 10–30 mol% Y, whereas they increased drastically for the copolymer with 40 mol% Y. The enzymatic degradation was estimated by the weight loss of the copolymer films in buffer solutions with a lipase at 37°C. The weight loss decreased remarkably with increasing Y and showed no weight loss for the copolymer with 40 mol% Y. On the other hand, the weight loss by alkali hydrolysis increased for the copolymers with 10 and 20 mol% Y, implying a difference in the degradation mechanism between enzymatic degradation and alkali hydrolysis.

INTRODUCTION

Since polymer wastes have caused serious problems of environmental destruction, there are increasing demands to develop biodegradable polymers. Among these, synthetic aliphatic polyesters are a promising class of biodegradable and hydrolyzable polymers [1-3], but they lack the general desirable thermal and mechanical properties needed for practical applications. However, introduction of a network structure into the backbone of polymer chains is expected to give them better physical properties than the corresponding linear polyesters. We have already reported on novel regular network polyesters [4-9] from multifunctional aromatic carboxylic acids and glycols or aromatic diols prepared by casting the prepolymers from solution followed by postpolymerization of the cast films. The resultant transparent, flexible, and insoluble polyester films showed some ordered structure and higher heat distortion temperatures compared with the corresponding linear polyester films. More recently, biodegradable regular network aliphatic polyesters have been prepared from glycerol and aliphatic dicarboxylic acids of various methylene chain lengths [10].

In this study we prepared network poly(ethylene adipate) copolymers copolymerized with trifunctional trimesic acid. The effect of comonomer content on thermal and mechanical properties as well as enzymatic degradation of copolymers was investigated.

EXPERIMENTAL

Monomers

Structural formulas and codes of the monomers used in this study are shown in Fig. 1. Adipic acid (6A) and trimesic acid (Y) were reagent grade and used as received. Ethylene glycol (2G) was distilled under reduced pressure. A copolymer is denoted by comonomer code. For example, a copolymer with 10 mol% Y is designated Y-10, where mol% Y = 100 × [mol Y/(mol Y + mol 6A)].

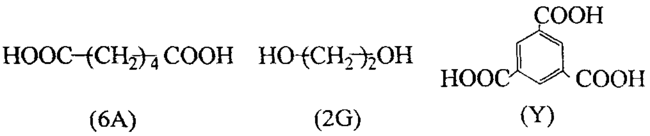

FIG. 1. Structural formulas and codes of monomers.

Preparation of Poly(Ethylene Adipate)

A mixture of 10 mmol adipic acid and 11 mmol ethylene glycol with tetraisopropyl titanate (ca. 0.5 wt% of total weight of reagent) as a catalyst was heated at 200°C for 3 hours in a stream of nitrogen and then heated at 230°C for 4 hours in a vacuum of 0.5-1.0 torr. The poly(ethylene adipate) (2G6A) prepared had a reduced specific viscosity of 1.33 dL/g in a 1% phenol/tetrachloroethane (60/40 by weight) solution at 30°C and had a melting temperature of 48°C as measured by a differential thermal analyzer.

Preparation of Prepolymers

As an example, Y-40 prepolymer was prepared as follows: A mixture of 4 mmol Y and 24 mmol 2G was heated at 200°C for 3 hours in a stream of nitrogen, then 6 mmol 6A was added, and further heated at 270°C for 10 minutes. The preparation conditions of the other prepolymers are given in Table 1.

Film Preparation and Postpolymerization

The obtained prepolymer was cast on an aluminum plate (size: 21 × 70 mm and 100 μm thick) from 14 wt% DMF solution and dried at 80°C for 2 hours. The cast film was postpolymerized under a stream of nitrogen at 260°C for 0.5-6 hours. After an aluminum substrate was dissolved off with 10% HCl solution, a transparent and flexible film was obtained which was insoluble in organic solvents. 2G6A homopolymer was melt-pressed and subsequently quenched in ice water.

Characterization

The infrared spectrum was recorded on a Jusco model IRA-1 spectrophotometer using a thin cast film of 10-20 μm thickness. The wide-angle x-ray intensity curve was determined with a Toshiba model ADG-301 x-ray diffractometer with nickel-filtered CuKα radiation. Density was measured in a KI aqueous solution at 30°C by the floating method [9]. Thermomechanical analysis (TMA) was performed in a penetration mode under a pressure of 10 kg/cm^2 and a heating rate of 20°C/min in a nitrogen atmosphere, using a Seiko model TMA thermomechanical analyzer. Tensile properties were measured with a Iwamoto tensile tester at an extension rate of 100%/min.

TABLE 1. Preparation Conditions of Prepolymers

Prepolymer code	6A, mmol	Y, mmol	2G, mmol	Preparation conditions
Y-10	9	1	21	200°C, 3 h → 270°C, 2 h
Y-20	8	2	22	200°C, 3 h → 270°C, 40 min
Y-30	7	3	23	200°C, 3 h → 270°C, 20 min
Y-40	6	4	24	200°C, 3 h → 270°C, 10 min

Enzymatic Degradation

The film specimen (film dimension 20 mm × 20 mm in size and about 120 μm thick) was placed in a small bottle containing 10 mL of 1/15 mol phosphate buffer solution (pH 7.2) with 20 mg *Rhizopus delemar* lipase (fine grade from Seikagaku Kogyo Co.). The bottle was then incubated at 37°C on standing for various times. After incubation the film was washed with water and dried overnight at room temperature in vacuo. The degree of degradation was estimated from the weight loss expressed by g/m^2, which was calculated by dividing weight loss by the area of copolymer films.

Alkali Hydrolysis

Alkali hydrolysis of the film specimen was carried out in a 5% NaOH aqueous solution at 40°C for 4 hours by the same procedure as above for enzymatic degradation.

RESULTS AND DISCUSSION

The degree of reaction was estimated from the infrared spectra of films. The network copolyesters showed infrared absorptions due to $-OH$ and $>CH_2$ groups at 3460 and 2959 cm^{-1}, respectively. The absorption at 3460 cm^{-1} decreased with increasing postpolymerization time, while the absorption at 2959 cm^{-1} remained unchanged. Since the postpolymerization proceeds through the elimination of the $-OC-O-(CH_2)_2-OH$ terminal group by the ester-exchange reaction, the change of absorption intensity ratio between hydroxyl and methylene groups is a measure of the degree of reaction.

For the copolymer with a molar fraction of n (n is a molar fraction of the Y component) at the initial stage of polymerization, the ratio of hydroxyl and methylene groups in a monomeric unit of $(CH_2)_4(COO(CH_2)_2OH)_2$ and $Ph(COO(CH_2)_2OH)_3$, $[OH]/[CH_2]$, is $(2 + n)/(8 - 2n)$, and varies with the progress of reaction to become $[(2 + n) - (2 + n)/(8 - 2n) - (4 - n)]$ when the network structure is completely developed. Thus the following equation is defined:

$$[OH]/[CH_2] = (2 + n - y)/(8 - 2n - y) \tag{1}$$

where y is the number of reacted functional groups. Then

$$y = ((2 + n) - (8 - 2n)\,[OH]/[CH_2])/(1 - [OH]/[CH_2]) \tag{2}$$

The degree of reaction D_R is calculated as

$$D_R = y/(2 + n) \times 100(\%) \tag{3}$$

y is determined from the measured absorption intensity ratio by using the calibration curve obtained for various diols and alcohols [6]. D_R values of copolymer films made using a postpolymerization temperature of 260°C and various postpolymerization times are summarized in Table 2. D_R values for copolymers increase and level out after 4-6 hours with increasing postpolymerization time. D_R of copolymers have a relatively high value of about 90% after 6 hours.

TABLE 2. Degree of Reaction of Network Copolyester Films at a Postpolymerization Temperature of 260°C

Polymer code	Postpolymerization time, hours	Degree of reaction, %
Y-10	6	93
Y-20	0.5	26
	1	79
	2	82
	4	90
	6	92
Y-30	0.5	79
	1	87
	2	89
	4	89
	6	90
Y-40	6	88

Figure 2 shows wide-angle x-ray scattering (WAXS) intensity curves of 2G6A homopolymer, copolymers, and 2GY (Y-100) prepared from Y and 2G [5]. 2G6A homopolymer film exhibits a distinct crystalline pattern, whereas copolymer films show only amorphous peaks, demonstrating crystallinity of the polymer, are largely destructed by incorporation of the Y component. However, the intensities of these amorphous peaks become higher with increasing Y, suggesting the formation of more ordered network structures. The densities of films were 1.236, 1.225, 1.226,

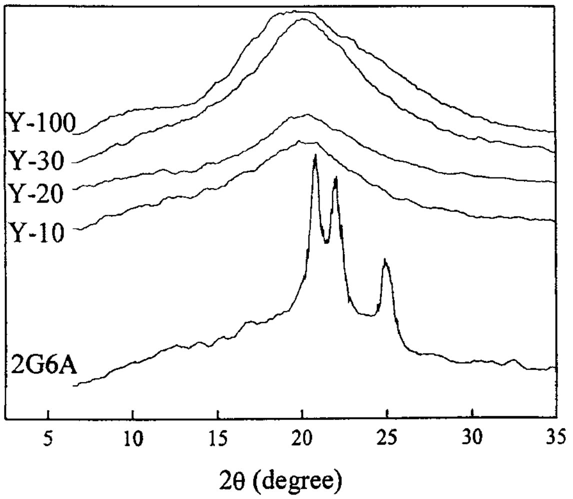

FIG. 2. WAXS curves of 2G6A homopolymer, 2GY homopolymer, and copolymer films postpolymerized at 260°C for 6 hours.

1.234, and 1.284 g/cm^3 for 2G6A homopolymer, Y-10, Y-20, Y-30, and Y-40, respectively. The density is lowered by the incorporation of Y, which may be caused by the decrease of crystallinity shown in Fig. 2. However, the densities increase drastically for Y-40 film, which can be explained not only by the higher concentration of the heavy benzene ring, but also by the increased crosslinking density. Thus, Y-100 has a density of 1.395 g/cm^3 [8].

Figure 3 shows TMA curves of Y-20 film. The heat distortion temperature, T_h, the inflection point of the curve, is observed in the TMA curve. The T_h values increase with increasing postpolymerization time, which corresponds to the change of D_R shown in Table 2. Complete penetration of the probe due to thermal decomposition of the film is observed below 100°C on films postpolymerized for shorter times, while a longer postpolymerization time enhances thermal stability greatly up to around 250°C due to extention of the polymer network structure. Table 3 gives T_h values for films postpolymerized for 6 hours. T_h is enhanced drastically by the incorporation of Y, which can be explained by the formation of a network structure as well as by an increase of the concentration of the rigid benzene ring.

Tensile properties for films postpolymerized for 6 hours are summarized in Table 4. Tensile strength and Young's modulus decrease rapidly by the incorporation of Y, but it is interesting that a dramatic increase is observed for Y-40 film, reflecting a much increased crosslinking density. Elongation also decreases with increasing Y due to the increased crosslinking density.

Figure 4 shows the enzymatic degradation of Y-10 film postpolymerized for 6 hours against the time of degradation at 37°C. A fresh lipase was used every 2 days.

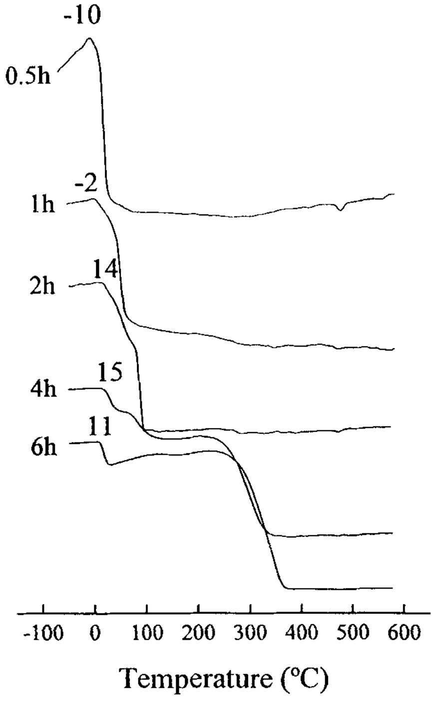

FIG. 3 TMA curves of Y-20 film postpolymerized at 260°C for various times.

TABLE 3. Heat Distortion Temperature of Films Postpolymerized at 260°C for 6 hours

Polymer code	T_h, °C
2G6A	−83
Y-10	−9
Y-20	11
Y-30	36
Y-40	48

TABLE 4. Tensile Properties of Films Postpolymerized at 260°C for 6 hours

Polymer code	Tensile strength, kg/mm^2	Young's modulus, kg/mm^2	Elongation, %
2G6A	0.96	33	263
Y-10	0.17	1.5	111
Y-20	0.27	3.6	116
Y-30	0.92	8.1	124
Y-40	2.33	79	32

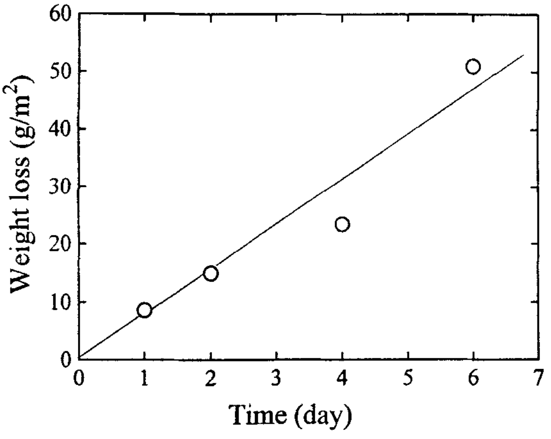

FIG. 4. Weight loss of Y-10 film against degradation time in the buffer solution of lipase at 37°C.

TABLE 5. Weight Loss by Enzymatic Degradation and by Alkali Hydrolysis for Films Postpolymerized at 260 °C for 6 hours

Polymer code	Weight loss, g/m^2		
	Lipase	Control	Alkali
2G6A	Degrades[a]	2	10
Y-10	51	3	17
Y-20	13	2	16
Y-30	3	0.3	2
Y-40	0	0	1

[a] The film disappeared after 24 hours of incubation.

The weight loss increases almost linearly. Table 5 shows the dependence of the weight loss for films degraded for 6 days at 37 °C on the composition of the copolymer. The weight losses of films are much larger than those of films without a lipase (control). 2G6A homopolymer film degraded very rapidly and disappeared after a 24-hour incubation period. Weight loss decreases remarkably by the incorporation of Y, and the Y-40 film shows no weight loss, corresponding to the drastic increase of density and tensile strength described above, which would be caused by increased crosslinking density and/or decreased concentration of enzymatically degradable aliphatic ester linkages.

Alkali hydrolysis of copolymer films was carried out in comparison with the above enzymatic degradation. The results are also shown in Table 5. Weight loss increases significantly by incorporation of Y, which may be caused by the large depression of crystallinity of copolymers as shown in Fig. 2. This behavior is different from that of the enzymatic degradation described above, implying a difference of the degradation mechanism between enzymatic degradation and alkali hydrolysis. Further studies on the enzymatic degradation mechanism are in progress. The decrease in weight loss at higher Y can be ascribed to a much increased crosslinking density and/or a decreased concentration of aliphatic ester linkages.

CONCLUSION

The above results show that thermal and mechanical properties as well as the rate of enzymatic degradation of copolymers can be varied widely by the Y content. The dramatic increase of T_h upon incorporation of Y makes these network polyesters promising as biodegradable polymers with enhanced thermal properties.

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