Synthesis, Characterization, and Enzymatic Degradation of Novel Regular Network Aliphatic Polyesters Based on Pentaerythritol

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ABSTRACT: Novel regular network polyesters were prepared from pentaerythritol (Xp) and aliphatic dicarboxylic acids of different numbers of methylene groups ($HOOC(CH_2)_{n-2}COOH$, $n = 4, 6, 8, 9, 10, 12, 14, 16$, and 20). Prepolymer prepared by melt polycondensation was cast from dimethylformamide solution and postpolymerized at 270 °C for various times to form a network. The resultant films were transparent, flexible, and insoluble in organic solvents. The network polyesters obtained were characterized by infrared absorption spectra, wide angle X-ray diffraction analysis, density, thermomechanical analysis, differential scanning calorimetry, tensile test, water absorption, and alkali hydrolysis. The enzymatic degradation estimated by weight loss of the network polyester films in a buffer solution of various kinds of lipases at 37 °C was studied. The enzymatic degradation of Xp*n* films was compared with that of the network polyester films of glycerol with various aliphatic dicarboxylic acids reported earlier.[12] After a 6 day incubation in *Rhizopus delemar* lipase solution, the weight loss was hardly observed for Xp4−8, while it increased gradually for Xp9−14 and showed the maximum weight loss of 13 g/m^2 for Xp14; then the weight loss decreased abruptly for Xp16−20. Other lipases of porcine pancreas and *Candida rugosa* hardly degraded Xp*n* films.

Introduction

In recent years much interest has been paid to the biodegradable synthetic polymers, because waste polymers have caused serious environmental problems. Synthetic aliphatic polyesters are one of the promising class of biodegradable polymers.[1−3] Aliphatic polyesters including copolyesters such as poly(ϵ-caprolactone)[4,5] and poly(1,4-butanediol succinate)[6] show excellent biodegradability, but they do not usually satisfy suitable thermal and mechanical properties when they meet the practical usages. The incorporation of network structure into the backbone is expected to give better physical and chemical properties such as resistance to heat distortion and resistance to chemicals. In fact several network polyesters with the much higher resistance to heat distortion than the corresponding linear polyesters have been prepared from multifunctional carboxylic acids and glycols.[7−11]

In the previous paper we reported the preparation and enzymatic degradation of regular network polyesters from glycerol (Yg) and various aliphatic dicarboxylic acids with different numbers of methylene groups (n).[12] It was found that *Rhizopus delemar* lipase remarkably degraded Yg8, Yg9, Yg10, and Yg12 network polyesters from Yg and dicarboxylic acids with the number of methylene groups of 6, 7, 8, and 10. In this study, the regular network polyesters were prepared from pentaerythritol and various aliphatic dicarboxylic acids with different numbers of methylene groups. The effects of the number of methylene groups on the structure and thermal, mechanical, and physicochemical properties as well as enzymatic degradation were investigated in comparison with the corresponding regular network polyesters from glycerol.[12]

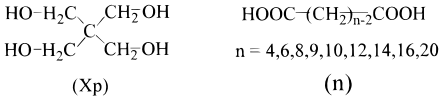

Figure 1. Structural formulas and codes of monomers used in this study.

Experimental Section

Monomers. Structural formulas and codes of monomers used for novel network polyesters are shown in Figure 1. Aliphatic dicarboxylic acids with different numbers of methylene groups (n) and pentaerythritol (Xp) were used as received.

Preparation of Prepolymers. All prepolymers were prepared by bulk polymerization. A mixture of 20 mmol of dicarboxylic acid and 10 mmol of pentaerythritol was put into the Pyrex glass tube equipped with a nitrogen inlet and a condensate collector. It was heated in a silicon oil bath from room temperature to 240 °C at a rate of about 5 °C/min under a stream of nitrogen and then maintained for 1−5 min (depending on the number of methylene groups in the dicarboxylic acid). Further heating caused the gelation of the prepolymers. After the glass tube was taken from the oil bath, it was cooled to room temperature.

Film Preparation and Postpolymerization. The prepolymer obtained was cast on an aluminum plate from a 20 wt % dimethylformamide solution at 80 °C. The cast film was heated at 270 °C for various periods of time to form a network under a stream of nitrogen in a Toyo Chemical Industry model KT-2 electric furnace (50 mm i.d., 300 mm length) equipped with a quartz tube, which is controlled by an Okura Electric model EC 5600 temperature controller. After the aluminum was dissolved off in a 10% hydrochloric acid solution, a transparent and flexible film was obtained, which was insoluble in organic solvents for polyesters such as phenol/*sym*-tetrachloroethane (60/40 by weight) mixed solvent and *m*-

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cresol. The polyester films obtained were denoted using the monomer code; the polyester derived from Xp and the dicarboxylic acid *n* is designated Xp*n*.

Characterization. The infrared spectrum was recorded on a JASCO model IRA-1 spectrophotometer using a thin film. Wide angle X-ray scattering (WAXS) patterns of the films were measured with a Toshiba model ADG-301 X-ray diffractometer with nickel-filtered Cu Kα radiation. Differential scanning calorimetry (DSC) was performed using Perkin-Elmer DSC7 controlled by a 1020 TA workstation. It was operated at a heating rate of 5 °C/min in a nitrogen atmosphere. In order to provide the same thermal history, each sample was preheated from room temperature to 100 °C and rapidly cooled to −50 °C. Then the DSC scan was recorded by heating from −50 to +100 °C. Thermomechanical analysis (TMA) was performed in a penetration mode under a pressure of 10 kg/cm^2 and at a heating rate of 20 °C/min in a nitrogen atmosphere, using a Seiko Instruments Model TMA-100 themomechanical analyzer controlled by an SSC-5200 disk station. A tensile test was performed with an Iwamoto tensile tester at a strain of 100%/min to measure tensile strength, elongation, and Young's modulus. The averaged value for 5−10 specimens was employed. The density of the film was measured using a sink and float method in potassium iodide aqueous solution at 30 °C. Water absorption was measured by immersing the film in water at 30 °C for 24 h, and then the specimens were taken out for weighing. Samples were gently blotted with filter paper prior to the weighing to remove surplus surface water and were dried to a constant weight. The water absorption of the films was evaluated as follows: Water absorption (%) = $100(W - W_0)/W_0$, where W_0 is the dry weight and W is the wet weight.

Enzymatic Degradation. The enzymes used in this study are lipases from *R. delemar* (specific activity of 600 unit/mg from Seikagaku Kogyo Co., Ltd.), *Candida rugosa* (specific activity of 720 unit/mg from Sigma Chemical Co., Ltd.), and porcine pancreas (specific activity of 179 unit/mg from Sigma Chemical Co., Ltd.).

The film specimen (20 mm × 20 mm, about 120 μm thickness) was placed in a vial containing 10 mL of $^1/_{15}$ mol of phosphate buffer solution (pH 7.2) with and without 20 mg of the above lipase. The vial was incubated at 37 °C for various periods of time. The phosphate buffer/enzyme solution was replaced every 48 h to keep the enzyme activity at the desired level throughout the experiment duration. After incubation, the film was washed extensively with water and dried at 80 °C *in vacuo* until a constant weight was reached. The degree of degradation was estimated from the weight loss expressed as g/m^2. The weight loss averaged for two specimens was employed.

Alkali Hydrolysis. Alkali hydrolysis of the film specimen was performed in a 5% sodium hydroxide aqueous solution at 40 °C for 4 h. The degree of alkali hydrolysis was also estimated from the weight loss using the same procedure as in the case of enzymatic degradation.

Results and Discussion

Degree of Reaction of Network Polyester Films. Figure 2 shows the IR spectra of the Xp10 film postpolymerized at 270 °C for various periods of time. The absorption at 3460 cm^{-1} due to the hydroxyl group decreases remarkably with increasing postpolymerization time, while the absorption at 2960 cm^{-1} due to the methylene group remains unchanged. Since the postpolymerization proceeds through the reaction between the hydroxyl group of pentaerythritol and the carboxyl group of dicarboxylic acids,[13] the change of absorption intensity ratio between the −OH and $-CH_2$ groups, A_{OH}/A_{CH_2}, is a measure of the degree of reaction. For Xp10, at the beginning of the reaction, the ratio of hydroxyl and methylene groups in a monomeric unit, [OH]/[CH_2], is 4/20 and varies with the progress of reaction to become 0/20 when the network structure has

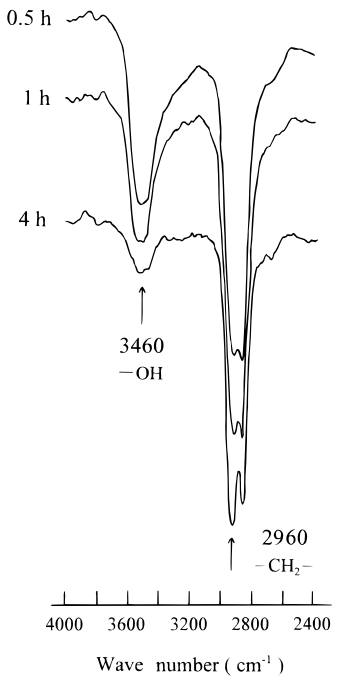

Figure 2. Infrared absorbance change of films at a fixed postpolymerization temperature of 270 °C for various postpolymerization times.

Table 1. Degree of Reaction of Films Postpolymerized at 270 °C

polym code	postpolym time (h)	deg of reacn (%)
Xp10	0.5	58
	1	71
	2	84
	4	86
	6	81
Xp4	4	63
Xp6	4	65
Xp8	4	89
Xp9	4	89
Xp12	4	90
Xp14	4	90
Xp16	4	90
Xp20	4	91

completely developed. Thus, the following equation is defined:

$$[OH]/[CH_2] = (4 - y)/20$$

and

$$y = 4 - 20\,[OH]/[CH_2]$$

where y is the number of reacted carboxyl groups. The extended general expression for an Xpn film is

$$y = 4 - 2n[OH]/[CH_2]$$

The degree of reaction (D_R) is calculated as

$$D_R = (y/4) \times 100\ (\%)$$

To obtain the quantitative [OH]/[CH_2] ratio in network films, the calibration curve between A_{OH}/A_{CH_2} made by the known diols and alcohols was used.[9] D_R values of network polyester films are summarized in Table 1. D_R values for Xp10 increase with increasing postpolymerization time and show a maximum value of 86% for Xp10 for 4 h. The decrease of the D_R value after 6 h may be caused by the thermal decomposition of the

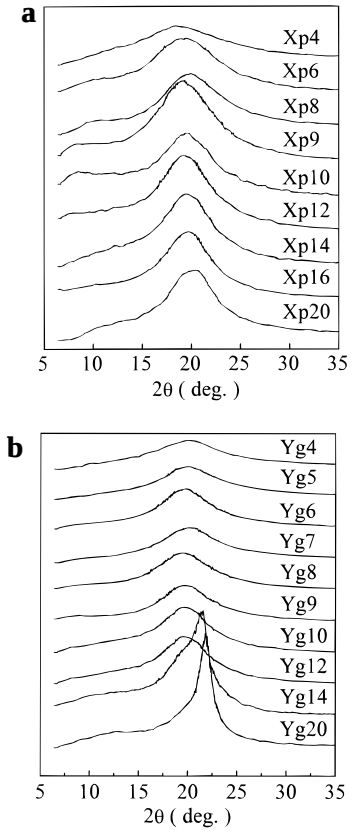

Figure 3. WAXS patterns of Xp*n* films (a) and Yg*n* films (b).

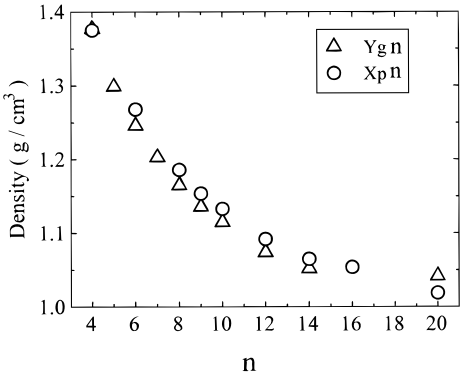

Figure 4. Comparison of the density change of Xp*n* films with Yg*n* films.

polymer. Thus the films postpolymerized at 270 °C for 4 h were used for their characterizations and enzymatic degradations unless otherwise noted. The D_R value is almost 90% irrespective of the number of methylene groups except for 63−65% for Xp6 and Xp4.

Structure of Postpolymerized Films. Figure 3 shows WAXS intensity curves of Xp*n* films (a) and the corresponding network polyester films (b) prepared from glycerol (Yg) and aliphatic dicarboxylic acids postpolymerized at 230 °C for 4 h[12] (referred to hereinafter as Yg*n* films). Two diffraction peaks were previously obtained for regular network aromatic polyesters,[4−8] suggesting the formation of some ordered structure owing to the regular network by the symmetric structure of the multifunctional monomers. A distinct single diffraction peak appears at ca. 20° for all the Xp*n* films and for Yg4−12 films, which also implies the formation of some ordered structure for these netwok aliphatic polyesters. Peaks are sharper for Xp*n* films than for the corresponding Yg*n* ones, showing the formation of more ordered network structure owing to the more

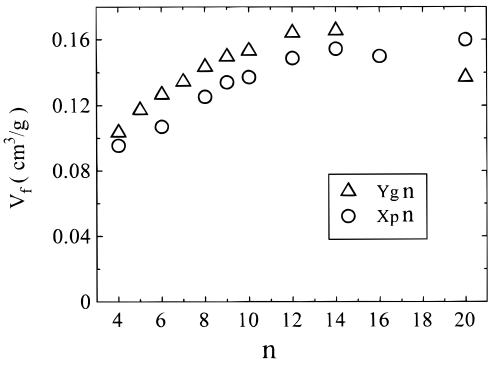

Figure 5. Comparison of the free volume change of Xp*n* films with Yg*n* films.

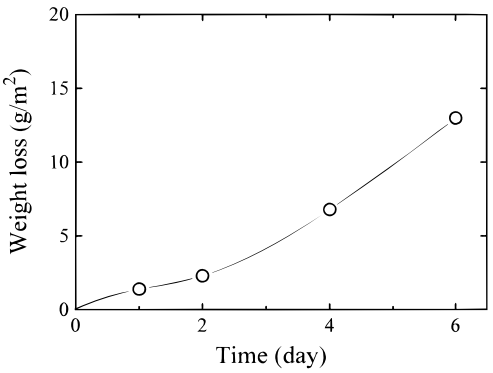

Figure 6. Weight loss of Xp14 film against degradation time in a lipase buffer solution at 37 °C.

symmetric pentaerythritol moiety. For Yg14 and Yg20, another sharper diffraction peak appears at around 21.5°, suggesting the crystallization of films, which is discussed below in relation to the results of a DSC scan.

Figure 4 shows the plots of density versus the number of *n* for Xp*n* films and Yg*n* films. The densities decrease for both films gradually with increasing *n*, suggesting an increase of the free volume of the network caused by extension of the length between the cross-linked sites. Thus the free volume of the network (V_f) for both films was estimated from the measured density (ρ) shown in Figure 4 according to the following equation:[14]

$$V_f = 1/\rho - 1.3V_w/M$$

where V_w is the summation of the group contribution of Van der Waals molar volume (cm^3/mol) and M is the molecular weight of the repeating monomeric unit (g/mol). V_f values estimated are plotted against the number of *n* in Figure 5. As expected, V_f increases gradually with increasing *n* except for the case of Yg20, which is probably due to the crystallization of the film.

Enzymatic Degradation of Postpolymerized Films. Figure 6 shows the dependence of the enzymatic degradation of the Xp14 film on degradation time at 37 °C in a buffer solution with *R. delemar* lipase. Weight loss increases nonlinearly with time. Blank experiments without lipase were performed in parallel in buffer solution at 37 °C. No weight loss was observed after a 6 day incubation in a blank test.

Figure 7 shows the number of methylene group dependence of weight loss after a 6 day incubation for Xp*n* films in *R. delemar* lipase solution and in porcine pancreas lipase solution. Figure 8 shows the same plots after 2 h incubation for Yg*n* films in both lipase solutions. The films with shorter methylene chains

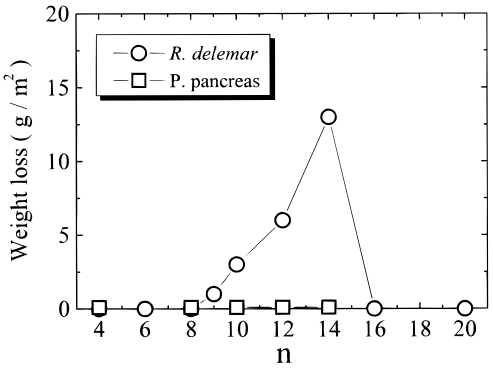

Figure 7. Weight loss change of Xp*n* films degraded in a lipase buffer solution for 6 days at 37 °C.

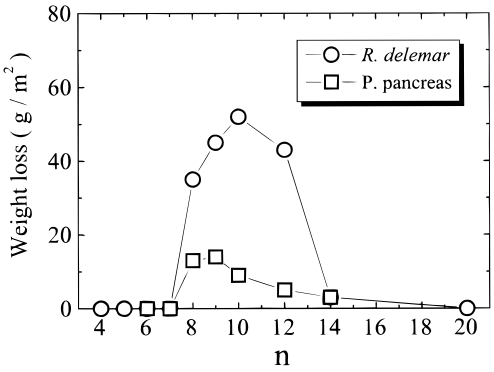

Figure 8. Weight loss change of Yg*n* films degraded in a lipase buffer solution for 2 h at 37 °C.

(Xp4−8 and Yg4−7) show no weight loss, suggesting the difficulty for penetrating lipase into the network film owing to the smaller network size. In *R. delemar* lipase solution, weight loss increases greatly for Xp9−14 and for Yg8−12 and showed the maximum value of 13 g/m^2 for Xp14 and 52 g/m^2 for Yg10, respectively. An increase of network space with an increase of the chain length between cross-linked sites may enable the penetration of a lipase into the network, leading to the enzymatic degradation. Weight loss drastically decreases for both films with much longer methylene chains (Xp16−20 and Yg14−20). It is noted that the degradation rate of Yg*n* and Xp*n* by *R. delemar* lipase depends greatly on the methylene chain length of the dicarboxylic acids. Similar behaviors have been observed for triglycerides of fatty acids with different numbers of methylene groups.[15] Porcine pancreas lipase degrades Yg*n* films, but not Xp*n* films. This lipase seems to preferentially degrade Yg*n* films with shorter methylene chains, which is consistent with the fact that it degrades the triglyceride of fatty acids with shorter methylene chains.[16] The decrease of the enzymatic degradation rate for Yg14−20 is partly related to the crystallite morphology of these samples. *C. rugosa* lipase did not degrade both films. The remarkable difference of degradation rate between Xp*n* and Yg*n* films is observed in *R. delemar* lipase solution. The degradation period time of 2 h is enough to decompose Yg*n* films because some of them were fragmented after 4 h incubation, whereas it takes 6 days to considerably decompose Xp*n* films. The degradation rate for Xp*n* films is much slower than that of the corresponding Yg*n* ones, which may be responsible for the difference of the chemical structure between them.

Thermal, Mechanical, and Physicochemical Properties of Postpolymerized Films. Figure 9 shows some typical DSC scans of the Xp*n* films (a) with

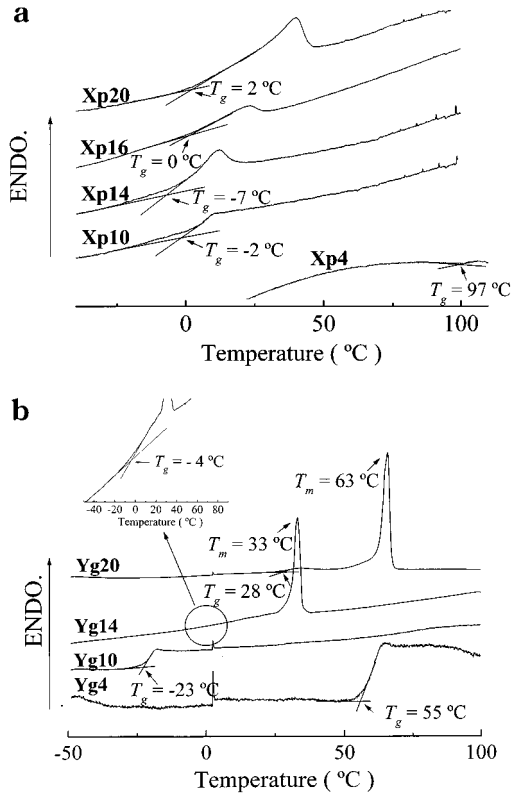

Figure 9. DSC profiles of Xp*n* films (a) and Yg*n* films (b).

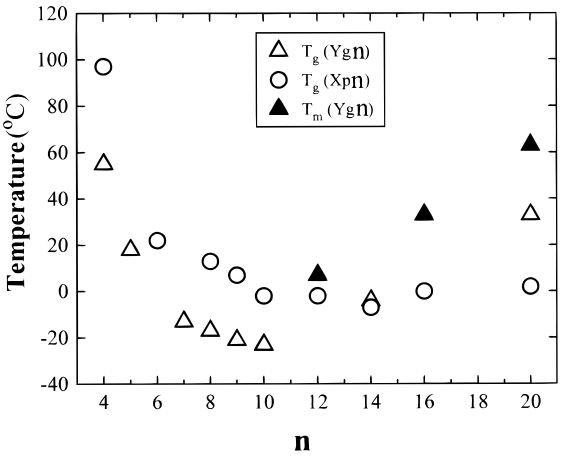

Figure 10. Comparison of glass transition temperatures (T_g) and melting temperatures (T_m) of Xp*n* films with Yg*n* films.

Yg*n* films (b). An endothermic transition due to glass transition (T_g) is observed for both series films. T_g values obtained are plotted against the number of *n* in Figure 10. For Xp*n* films, T_g decreases with increasing *n* and levels out above $n = 10$. T_g for Yg*n* films also decreases with increasing *n*, shows the minimum value of −23 °C for Yg10, and then increases with *n*. The decrease in T_g with increasing *n* corresponds to the increase of free volume shown in Figure 5.

An endothermic transition also appears for the Yg*n* films with the longer methylene unit probably due to the crystallization of the methylene unit in the dicarboxylic acids. The melting peaks for Yg14 and Yg20 correspond to the sharp X-ray diffraction peaks at 21.5° in Figure 3b. T_m observed in the DSC scans are also plotted in Figure 10. T_m increases with the increasing number of methylene groups, which is consistent with the fact that T_m for aliphatic linear polyesters increases with the increasing number of methylene groups.[17] It

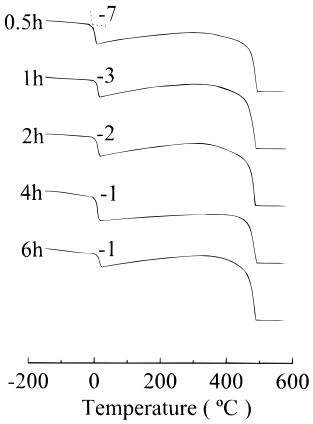

Figure 11. TMA profiles of the Xp10 film at 270 °C for various postpolymerization times.

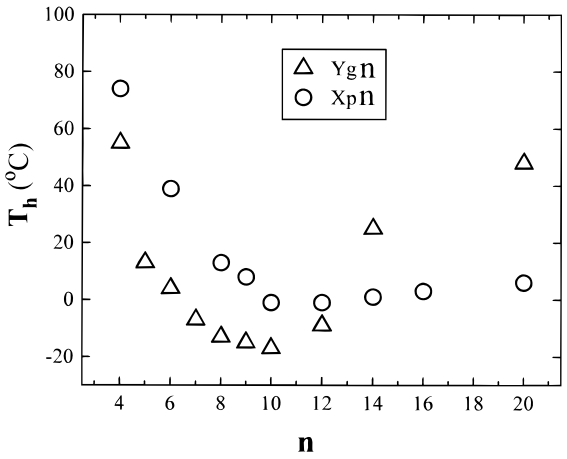

Figure 12. Comparison of the heat distortion temperature (T_h) of Xp*n* films with Yg*n* films.

Table 2. Tensile Properties of Xp*n* Films

polym code	tensile strength kg/mm^2)	elongation (%)	Young's modulus (kg/mm^2)
Xp4	4.0	3	198
Xp6	1.6	4	77
Xp8	1.3	42	13
Xp10	0.2	46	0.7
Xp14	0.6	65	0.5
Xp20	0.6	73	1.3

is noteworthy that the crystallization occurs for network polyesters. Further study on this interesting phenomenon is in progress and will be reported in detail in the future.

Figure 11 shows TMA curves for Xp10 film postpolymerized at 270 °C for various times. The heat distortion temperature (T_h), the inflection point of the TMA curve, increases with increasing postpolymerization time and levels off above 4 h,which corresponds to the increase of the D_R value as seen in Table 1. The TMA probe penetrates the film completely in the vicinity of 500 °C due to thermal decomposition. Figure 12 shows dependence on the number *n* in Xp*n* films with the Yg*n* films. The plot profile of T_h versus *n* corresponds well to that of T_g versus *n* shown in Figure 10.

Tensile properties are summarized for Xp*n* films in Table 2. The tensile strength and Young's modulus decrease drastically with the increasing number of methylene groups and almost levels out at $n \geq 10$, corresponding well to the profile of T_h shown in Figure 12. The extremely larger Young's modulus for the Xp4 would be due to the higher T_g value in Figure 10. The elongation increases with the increasing number of methylene groups, which is ascribed to the increased network free volume shown in Figure 5.

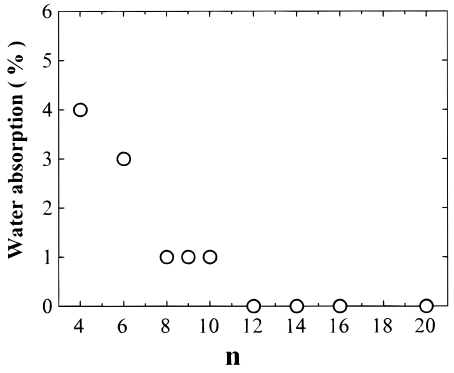

Figure 13. Water absorption change of Xp*n* films.

Figure 13 shows the dependence of water absorption on *n* for Xp*n* films. The water absorption decreases with increasing *n* and almost becomes zero at Xp12−20. The much higher water absorption of Xp4 and Xp6 may be ascribed to the higher content of unreacted terminal hydroxyl and/or carboxylic groups, which is consistent with lower D_R values, as shown in Table 1.

The alkali hydrolysis of Xp*n* films was carried out to compare with the enzymatic degradation described above. No weight loss was observed for Xp8−20, while the weight loss was 6 and 16 g/m^2 for Xp4 and Xp6, respectively, corresponding to the higher water absorption of these films shown in Figure 13. The nature of the alkali hydrolysis and water absorption is not directly related to the enzymatic degradation.

Conclusions

Novel regular network polyesters of pentaerythritol and various aliphatic dicarboxylic acids with different numbers of methylene groups were prepared for biodegradable polyesters. It was found that Xp8−14 were degraded by *R. delemar* lipase and Xp14 showed the largest weight loss after a 6 day incubation. A remarkable dependence of enzymatic degradation on the methylene chain length appeared for Xp*n* as well as Yg*n*, which was similar to that of triglyceride of fatty acids with different numbers of methylene groups. Porcine pancreas lipase degraded Yg*n*, but hardly Xp*n*, and *C. rugosa* lipase degraded neither film.

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tion between pentaerythritol molecules should not be considered. Thus the decrease of absorption at 3460 cm^{-1} is solely ascribed to the water elimination reaction between the hydroxyl group and diacid group.

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