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SYNTHESIS AND CHARACTERIZATION OF CROSSLINKED POLYMERS FOR BIOMEDICAL COMPOSITES

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ABSTRACT

Three kinds of low molecular weight unsaturated polyesters containing carbon-carbon double bonds were synthesized by the reaction of poly-(ϵ-caprolactone) diol or *D,L*-lactide and glycolic acid with maleic anhydride or fumaric acid. These functionalized polymers were thermally crosslinked in the presence of radical initiator to prepare the crosslinked polymers available as a matrix resin for biomedical composites. Hydrolysis of the crosslinked polyesters was investigated in buffer solution at 37°C.

INTRODUCTION

Research and development of biodegradable and bioabsorbable materials for use as temporary replacement for fractured bone or lost soft tissue has been an objective of many workers for many years [1-4]. Although metallic devices such as plates, screws, and rods have been traditionally used in osteoplasty for internal fixation, basically they have two serious problems: one is osteoporosis

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due to stress-protection atrophy [5] and the other is that these nondegradable devices require a second surgical operation for their removal after the bone is healed. To alleviate these problems, investigations have been carried out on both biostable and completely bioabsorbable composite implants, for which polyesters from lactic and glycolic acids have been mainly used as degradable matrix resins [6, 7]. However, it was also reported that these thermoplastics have inherent difficulties in interfacial wetting with reinforcing fibers, which limits optimum stress transfer between fiber and matrix [2].

To improve the disadvantages caused by linear thermoplastics, we have investigated the possibility of using crosslinked polyester thermosetting resins as the matrix for the composite bone plate [8, 9]. Earlier investigations on cross-linked poly(ϵ-caprolactone) have also pointed to crosslinking as one factor that impacts on the degradation rate [10-12].

In this work we present synthesis and crosslinking of oligomeric crosslinkable unsaturated polyesters and degradation results for their crosslinked polymers in buffer solution.

EXPERIMENTAL

Materials

The following were obtained from Aldrich Chemical Co.: polycaprolactone-diol(PCL-diol: MW 530) was dried *in vacuo* for 2 d prior to use; glycolic acid (Gold Label) was used as received; *cis*-2-butene-1,4-diol was distilled under reduced pressure; zinc stearate and stannous octoate were used as received; maleic anhydride (MAn) and fumaric acid were purified by sublimation; styrene, methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA), methyl acrylate (MA), and all solvents were distilled before use; benzoyl peroxide (BPO) was recrystallized from chloroform.

D,L-Lactide from Polyscience Chemical Company was sublimed at 100°C under vacuo.

Instrumentation

Proton magnetic resonance spectra (^{1}H NMR) were recorded on either a Varian EM 360-MHz or an IBM WP-200 SY FT-NMR. Infrared spectra (IR) were obtained from a Nicolet 60SX FTIR. Thermal data of all polymers were measured on either an Omnitherm QC-25 or a Perkin-Elmer Model DSC-2 at a 20°C/min heating rate under nitrogen purge.

Synthesis of PCL-Dimaleate

Into a 500-mL 3-necked flask, equipped with a reflux condenser and thermometer, were placed 20 g PCL-diol, 8.16 g MAn, 0.13 g zinc stearate as a catalyst, and 250 mL of freshly distilled toluene. The mixture was refluxed for 24 h. After the reaction was completed, the solvent was removed under reduced pressure to give a viscous crude product. Large amounts of carbon tetrachloride and distilled water were added, followed by vigorous stirring. The solution was separated into three layers through a separatory funnel. The yellow viscous oil in the middle layer was collected and then dissolved in an excess of chloroform. Anhydrous magnesium sulfate was poured into the solution to remove traces of water, then filtered off. The chloroform was distilled off to obtain the product, PCL-dimaleate, in high yield (80%).

Crosslinking of PCL-Dimaleate

PCL-dimaleate was dissolved in tetrahydrofuran (THF) to give a 33.3 wt% solution. To the solution (6 g) was added a predetermined amount of radical initiator, which was stirred until it dissolved. The solution was poured into a 5-cm Petri dish and placed in an oven at 75°C for the desired time under argon to make a crosslinked film. The crosslinked film was extracted with TMF for 24 h in a Soxhlet extractor to remove all residues from the reaction as well as uncrosslinked PCL-dimaleate.

Preparation and Crosslinking of Highly Unsaturated PCL

Into a 50-mL flask with attached gas inlet and outlet were added PCL-dimaleate (10 g, 1.6 mmol), PCL-diol (8.43 g, 16 mmol), and *p*-toluenesulfonic acid (0.037 g, 0.2 wt% of reactant) as a catalyst. The flask was placed in a silicone-oil bath under argon purge for 24 h to give highly unsaturated PCL. After polymerization, the highly viscous polymer was dissolved in chloroform and then precipitated by adding an excess of ethyl ether. The purified highly unsaturated PCL was filtered and then dried *in vacuo* at 40°C for 24 h. The specific viscosity of the highly unsaturated PCL was 0.08 dL/g, measured in a chloroform solution in a Cannon-Fenske viscometer at 25°C. The crosslinking of the polymer was carried out by the same procedure as that of PCL-dimaleate.

Synthesis of Butenediol/Lactate/Glycolate Oligomer

To a 500-mL 3-necked flask, equipped with mechanical stirrer, condenser, and argon inlet, were added 2-butene-1,4-diol (59.43 g, 0.67 mol), racemic

D,L-lactide (145.82 g, 1.01 mol), and glycolic acid (43.16 g, 0.57 mol). Stannous octoate (1.09 g, 2.7 mmol) at 0.4% based on butenediol was added. The flask was submerged into a silicone-oil bath thermostated at 100°C. After 4 h the temperature was increased to 120°C. After 21 h a vacuum of 1-2 torr was slowly attained and held for 4 h, at which time the pressure was reduced to 0.1-0.05 torr. The vacuum was held for an additional 5 h, then the flask was cooled. IR and ^{1}H-NMR spectra were recorded at this point.

Preparation of Oligomeric Unsaturated Polyester

Based on the theoretical molecular weight of 238 g/mol (assuming complete conversion and complete removal of water from the condensation reaction), butenediol/lactate/glycolate oligomer (1.0 mol) and fumaric acid (0.9 mol) were added to a 500-mL 3-necked flask equipped with a mechanical stirrer, gas inlet, and outlet. The flask was submerged in a preheated 160°C oil bath. After 40 h of condensate distillation, the temperature was maintained for 7 additional hours at 180°C. Then the melt was cooled to 165°C, and a 10-torr vacuum was slowly attained. After 16 h of this condition, the mechanical stirrer was removed and a final vacuum of 4 torr was applied for an additional 25 h. The polymer was then cooled, dissolved in chloroform, filtered, precipitated into cold methanol, filtered, and vacuum dried for 3 d at 50°C.

Preparation of Crosslinked Polyester Film

BPO (at concentrations of 0.1, 0.5, 1, 3, 5, 7, and 9 wt%) was added to 20 wt% solutions of oligomeric unsaturated polyester in THF. A 12-mL portion of each solution was poured into a 5-cm Petri dish. THF was evaporated at room temperature over a period of 24 h. Samples in Petri dishes were placed under an argon atmosphere over a hot plate and slowly heated to 70°C for 22 h, then the temperature was raised to 100°C for an additional 2 h. These films were used for thermal analysis evaluation.

A larger film was prepared on Teflon covered foil for hydrolysis studies. The foil was formed into a dish, and 20 wt% oligomeric solution was poured into it. The solvent was dried at ambient temperature for 24 h followed by slow evacuation in a vacuum oven at 40°C for another 24 h to give a void-free film. After 24 h the vacuum oven was back-purged with argon. The temperature was slowly brought to 70°C over a 1-h period and held for 13 h, then it was increased to 100°C for an additional 11 h. The film came out clear and void free.

Hydrolysis of Crosslinked Polyester Film

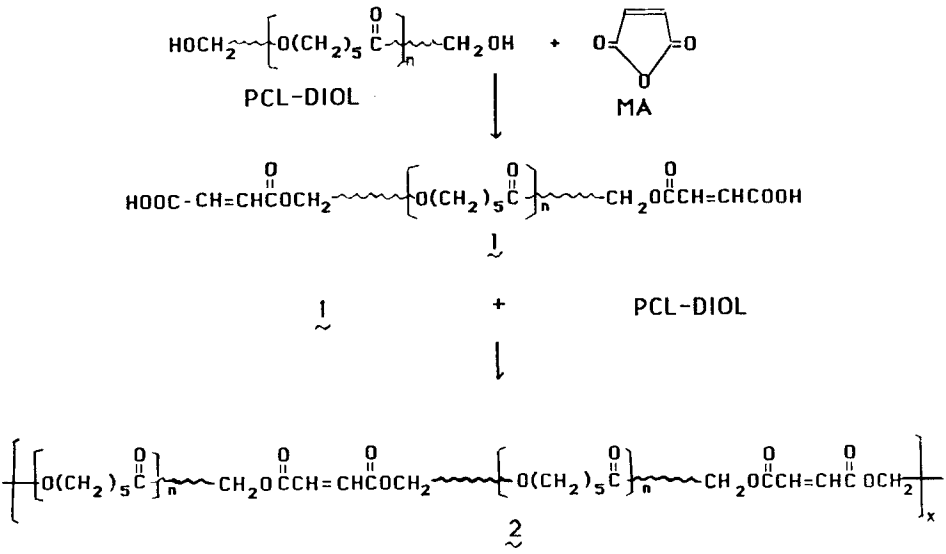
Crosslinked butene diol/lactate/glycolate/fumarate polyester film from 10 wt% BPO was cut into sections and weighed. Similar sections were prepared from amorphous poly(*D,L*-lactic acid) and crystalline poly(*L*-lactic acid) for comparison. Three buffer solutions, at pH 5.4, 7.4, and 10.0, were used. The pH 5.4 buffer solution was 0.05 *M* sodium and potassium phosphate. The pH 7.4 solution was also a phosphate buffer. The pH 10.0 solution was 0.05 *M* sodium borate and sodium carbonate. The pH 5.4 and 10.0 buffers were certified buffers from pHydrion Buffers, Micro Essential Laboratory. The pH 7.4 solution was made in-house. All pH values were checked with a Corning Model 130 pH-meter. Buffer solutions and all glassware were autoclaved. Sodium azide (0.02 wt%) was added to the buffer solutions to remove possible biological interference. Two samples of each of the three materials were put into test tubes with 20 mL each of buffer solution, for a total of 12 tubes. These were gently agitated on a shaker table inside a thermostat at 37°C. Samples were periodically weighted wet, vacuum dried for at least 24 h, and then weighed dry. This was performed at intervals of 1, 8, and 18 d. Buffer solutions were changed weekly, Before testing, all samples were stored in a desiccator.

RESULTS AND DISCUSSION

Synthesis and Crosslinking of Unsaturated PCL

Maleic anhydride was reacted with low molecular weight PCL-diol to give the PCL-dimaleate **1** containing crosslinkable carbon-carbon double bonds at both ends (Scheme 1).

The IR spectrum of the PCL-dimaleate shows a broad absorption band at about 3500 cm^{-1} due to the COOH end groups. At 3120 and 1632 cm^{-1} are olefinic CH and C=C stretching bands, which are not shown by PCL-diol. This indicates that the ring-opened moiety of the maleic anhydride was incorporated into the PCL. These results are consistent with the ^{1}H-NMR spectrum. The hydroxyl proton peak from PCL-diol disappears at 3.2 ppm, while the olefinic and the carboxylic acid proton at the two ends of PCL-dimaleate appear at 6.2 and 9.5 ppm, respectively. The carboxylic acid peak is shifted downfield compared to the usual carboxylic acid. This may be due to the intramolecular hydrogen bonding of the end group of PCL-dimaleate. The relative integration ratio between the characteristic protons in PCL-dimaleate indicates



SCHEME 1.

that one molecule of the ring-opened maleic anhydride is incorporated into both ends of PCL-diol.

Table 1 shows the effect of the concentration of radical initiator on the crosslinking reaction of PCL-dimaleate. The degree of crosslinking of PCL-dimaleate increased as the concentration of radical initiator increased up to 20 wt%. When LPO was used as a radical initiator, although the concentration of LPO was increased up to 20 wt%, the crosslinked polymers obtained were always opaque, rubbery, and tacky gels. This may be due to the low compatibility of the LPO with PCL-dimaleate, which results in a low degree of crosslinking. The extent of degree of crosslinking, which was calculated from the relative intensity of the 1738 and the 1632 cm^{-1} peaks due to ester and carbon-carbon double bonds, incorporated into PCL-dimaleate, depends considerably on the kind of initiator used. This result indicates that the compatibility of radical initiator with PCL-dimaleate is very important to the crosslinking reaction. In order to increase the compatibility, when BPO was used as a radical initiator instead of LPO, the resulting crosslinked polymers had a high degree of crosslinking even at low concentrations of BPO. Nevertheless, the apparent physical properties of the crosslinked film obtained were still rubbery and soft at room temperature.

TABLE 1. Crosslinking Reaction of PCL-Dimaleate by Radical Initiator[a]

Exp.	Initiator concentration, wt%		Time, h	Characterization of crosslinked PCL-dimaleate			
				Appearance	Apparent properties	Film forming[b]	Degree of crosslinking,[c] %
1	L.P.O.	20	36	Opaque	Rubbery, sticky gel	Δ	38.2
2		10	36	Opaque	Sticky, viscous liquid	X	20.6
3		5	48	Opaque	Sticky, viscous liquid	X	11.1
4		1	48	Clear	Sticky, viscous liquid	X	2.6
5	B.P.O.	20	36	Clear	Rubbery, film	○	58.5
6		10	36	Clear	Rubbery, sticky film	○	48.7
7		5	48	Clear	Rubbery, sticky gel	■	45.5
8		1	48	Clear	Viscous liquid	X	14.3

[a]Carried out by 33% PCL-dimaleate solution in THF at 75°C in vacuum oven under Ar.
[b]○, Good; ■, not good; Δ, bad; X, not formed.
[c]Calculated from the relative intensity ratio of C=O (1738 cm^{-1}) to C=C (1632 cm^{-1}).

TABLE 2. Crosslinking Reaction of Unsaturated-PCL by BPO in the Presence of Styrene (MMA or HEMA)[a]

Exp.	Unsaturated PCL, g		Styrene, g	BPO,[d] wt%	Characterization of crosslinked unsaturated-PCL: Appearance	Apparent properties	Film forming[h]	Extracted homopolymer,[e] %
9	PCL-dimaleate[b]	1.0	0.2	0.5	White, clear	Rubbery film	■	15
10		1.0	0.2	5.0	White, clear	Hard film	○	2.0
11		1.0	0.1	2.0	White, clear	Rubbery film	■	5.2
12[f]		1.0	0.2	5.0	White, clear	Hard film	○	1.8
13[g]		1.0	0.2	5.0	White, opaque	Hard, brittle film	○	30
14	Unsaturated-PCL[c]	2.0	0.2	2.0	Yellow, clear	Rubbery film	■	8.6
15		2.0	5.0	5.0	Yellow, clear	Hard film	○	4.5
16[f]		2.0	0.4	5.0	Yellow, clear	Hard film	○	6.2
17[g]		2.0	0.4	5.0	White, opaque	Hard film	○	20.5

[a]Crosslinking temperature, 75°C; time, 24 h.
[b]33% THF solution.
[c]20% THF solution.
[d][BPO] relative to [unsaturated PCL + crosslinking agent monomer].
[e]Calculated from Soxhlet extraction in THF for 24 h.
[f]MMA used as a crosslinking agent.
[g]HEMA used as a crosslinking agent.
[h]See Table 1 for symbols.

TABLE 3. DSC Data for Crosslinked Polymers[a]

Crosslinked polymer[b]	T_g,[c] °C
(PCL-diol)	(T_m, 35)
(PCL-dimaleate)	-55 (T_m, 25)
7	-42
10	-35
12	-36
13	-40
16	-38

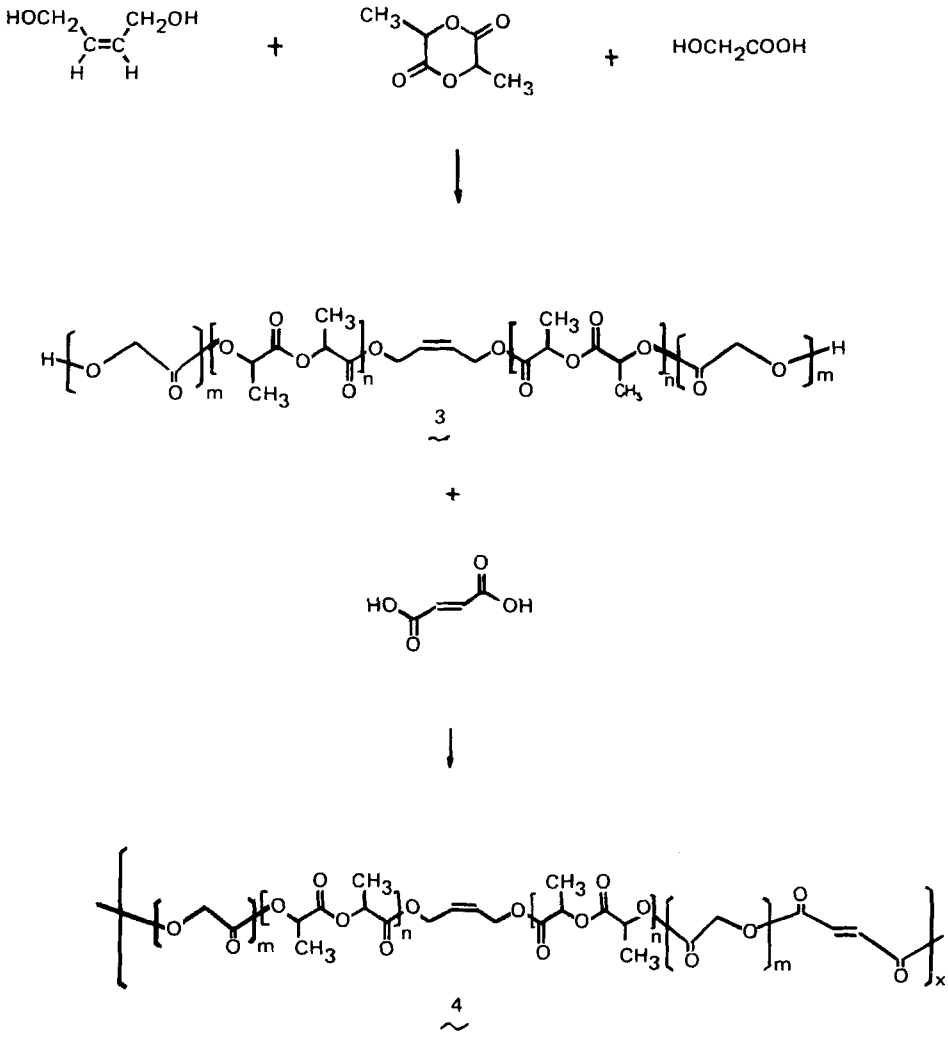
Highly unsaturated PCL (2 in Scheme 1) was synthesized and crosslinked by radical initiator. However, the properties of the resulting crosslinked polymer were also similar to those of the PCL-dimaleate. This may be due to two possible reasons. One is that the PCL-dimaleate radicals generated by radical initiator during crosslinking reaction are too stable to react with other double bonds; the other is that the mobility of the growing radicals is not enough to give a crosslink [13].

Accordingly, vinyl monomers, such as styrene, MMA, and HEMA, were used as comonomer and crosslinking agent in the presence of BPO to increase the extent of reaction with the unsaturated ester group (–OC–CH=CH–CO–) as well as to increase the T_g (Tables 2 and 3). As a result, both hard and transparent crosslinked polymers were prepared even at low concentrations of initiator. It is, therefore, considered that these crosslinked polymers may be used as matrix resins for biomedical composites. Although units of styrene and MMA are not desirable as part of degradable polymers, nontoxic and hydrophilic units, such as *N*-vinyl-2-pyrrolidone and HEMA, are most interesting as part of degradable polymers.

Table 3 summarizes the T_g data of the prepared crosslinked polymers in the presence of BPO as a radical initiator. The T_g increased by about 10 to 20°C by the introduction of crosslinks into oligomeric unsaturated polyesters.

Synthesis and Crosslinking of Unsaturated Polyester

2-Butene-1,4-diol was used as a difunctional initiator with stannous octoate as catalyst for the ring-opening polymerization of *D,L*-lactide, followed by



SCHEME 2.

condensation with glycolic acid to give a random butenediol/lactate/glycolate diol oligomer (**3** in Scheme 2). Subsequently **3** was chain extended by reaction with fumaric acid to give the unsaturated polyester **4**, butenediol/lactate/glycolate/fumarate oligomer.

After the first reaction step of condensing butenediol with lactide and glycolic acid, the IR spectrum shows a large OH absorbance. The hydroxy group absorption band is broad at 3430 cm^{-1}, and the ketone band shows at 1747 cm^{-1}. At 1424 cm^{-1} there is a peak from the glycolate CH_2 group. This assignment is inferred by the absence of this peak in the butenediol/lactate oligomer spectrum reported in our earlier work. All other aspects of the spectrum are very similar to that of the butenediol/lactate oligomer.

In the ^{1}H-NMR spectrum of butenediol/lactate/glycolate diol **3**, one broad singlet at 3.37 ppm is due to both glycolate and lactate hydroxyl end groups. Peaks for the lactate methine protons are downfield from peaks for the glycolate methylene protons, as reported previously [14]. End group glycolate methylene protons absorb at 4.19 ppm, and the signal for the interior ones is mixed with the signal for methylene protons of butenediol.

In the copolymerization of lactide and glycolide, the reactivity ratio is such that glycolide prefers to react with glycolide better than with lactide. Copolymers develop blocks of glycolate segments, separated by single lactate groups, until the glycolide is used up, when lactate blocks start to form toward the chain ends [14]. In the present work, lactide was copolymerized with less reactive glycolic acid. While the molecular weight obtainable is not as high, better randomness may be achieved by this method. The addition ratio of lactate units to glycolate units was 3.5:1 (1.75 lactides to 1 glycolic acid). The ^{1}H-NMR integration for the product indicated a ratio of 4.4:1 lactate to glycolate.

On further esterification of the butenediol/lactate/glycolate oligomer with fumaric acid, the IR shows a drastic increase in the ester group absorption at 1096 cm^{-1} at the expense of two bands at 1133 and 1050 cm^{-1} due to C–O associated with OH end groups. An olefin band appears at 1645 cm^{-1}, but it is uncertain whether this is the C=C from *cis*-2-butenediol. mono- or disubstituted fumarate, or fumarate isomerized to maleate. The C=O band is broader with a low energy shoulder due to the fumarate C=O. These assignments have also been confirmed by comparison with the spectrum for diethyl fumarate.

General simplification is noted in the ^{1}H-NMR spectrum on chain extension. The number of CH_3 proton peaks decreases, and there is almost complete elimination of peaks due to glycolate CH_2 and lactate CH with adjacent OH end group. The small peak area that remains indicates incomplete esterification, as does the fumarate olefin proton peak multiplicity in the 6.86-6.99 ppm region. The two olefin peaks at 6.99 and 6.94 ppm of approximately equal size are due to glycolate/fumarate ester, while those at 6.97 and 6.92 ppm, also of about equal size but larger than the glycolate/fumarate peaks, are

due to lactate/fumarate ester. The downfield lactate and glycolate ester peaks arise from fumarate ester, the upfield pair from olefinic protons adjacent to a carboxylic acid group. Exact integration is not possible, but it can be seen, at least qualitatively, that there is more lactate than glycolate. Also, it can be deduced that there is roughly three times more monosubstituted than disubstituted fumarate. Just upfield, at 6.87 ppm, there are small methyl fumarate peaks due to CH_3OH precipitation or the drying step of oligomer work-up.

DSC results for a series of crosslinked samples of the butenediol/lactate/glycolate/fumarate oligomer are shown in Table 4. With increasing BPO crosslink initiator, not only does the T_g increase, but also the width of the transition. The rapid initial change in T_g with % BPO reminds one of the rapid initial change in T_g with molecular weight, as seen with polystyrene [15]. With this unsaturated polyester, the change is only partially due to molecular weight increase. Since there is reactivity in the chain interior as well as at the chain ends, the effect must also be caused by decreased segment mobility on crosslinking. The crosslinked polyester films obtained were transparent, flat, and hard. Therefore, these crosslinked polyesters may be suitable as matrix resins for biomedical composites.

Hydrolysis Study

The crosslinked butenediol/lactate/glycolate/fumarate polyester from 9 wt% BPO was chosen for hydrolysis study in different buffer solutions. All samples for the hydrolysis study were thin, flat, rectangular pieces. The poly-

TABLE 4. DSC Results for BPO-Crosslinked Butene Diol/Lactide/Glycolate/Fumarate Polyester

Sample	Weight, mg	wt% BPO	T_g, °C	T_g width, °C
A	11.1	0	26	9
B	10.1	0.5	33	15
C	10.5	1.0	41	21
D	10.4	3.0	50	23
E	9.3	5.0	49	37
F	9.7	7.0	51	36
G	10.1	9.0	53	40

(*L*-lactic acid) samples appeared opaque/white and remained virtually unchanged throughout the test period. The poly(*D,L*-lactic acid) samples started clear/straw colored and turned opaque/white after 1 d, independent of pH. Every amorphous poly(*D,L*-lactic acid) sample became deformed and gradually assumed the shape of the bottom of the test tube. After 40 d the crosslinked sample in pH 5.4 buffer was opaque when wet but cleared on drying. The rest of the crosslinked samples remained clear/straw colored. Their shape was retained until they started to break apart.

After 8 d, internal voids could be seen by eye. The disk-shaped voids were most prominent in the pH 10.0 buffer, least in the pH 5.4 buffer. In Fig. 1, the 5.4 and 7.4 pH buffer samples are compared after 8 d immersion. The samples were still saturated at the time the photographs were taken. The voids parallel to the plane of the photograph appear as disks, while those perpendicular to the plane appear slits.

Figure 2 shows the pH 10.0 sample after 8 d by both regular illumination and under crossed polarizer and analyzer. The birefringence indicates stress at the void edges, suggesting a high degree of hydrostatic pressure. This has been seen in other studies on the degradation of crosslinked polyester resins in water and electrolyte solutions. Osmotically induced cracks increase the hydrolysis rate. Chemical processes, such as hydrolysis, interact synergistically with physical processes, such as swelling stress.

These samples were prepared by curing above their T_g in Teflon-coated foil pans. On cooling, some stresses may have been locked in, but since the pans were free to change shape and since the film separated from the edges of the pans, this locked-in stress on cooling was minimized. Even though the dry-sample T_g was above 37°C, due to plasticization by water, the test conditions were probably at a temperature that allows some segmental motion to relieve stress. Birefringence points to buffer solution forced into the crosslinked matrix. Carboxylic end groups, evidenced by ^{1}H NMR, may create a driving force to promote buffer diffusion.

Figures 3-5 and Table 5 show sample weight loss during a 40-d period. The PLLA samples have not lost any weight within experimental error. PDLLA loses a little, but the loss is marginal. The crosslinked samples do lose considerable weight. After 18 d the crosslinked samples in pH 10.0 degraded to the point of fragmentation into gelatinous pieces, as did the pH 7.4 samples after 40 d. By the end of this time it was apparent that the crosslinked material was more hydrolyzed by the more basic solutions. This agrees with results of Chu, who detected more hydrolysis of poly(glycolic acid) sutures in buffer solutions at pH 10.09 compared with buffers of pH 5.24 and 7.44 [16].

Figures 6-8 and Table 6 show the degree of buffer uptake. These weights

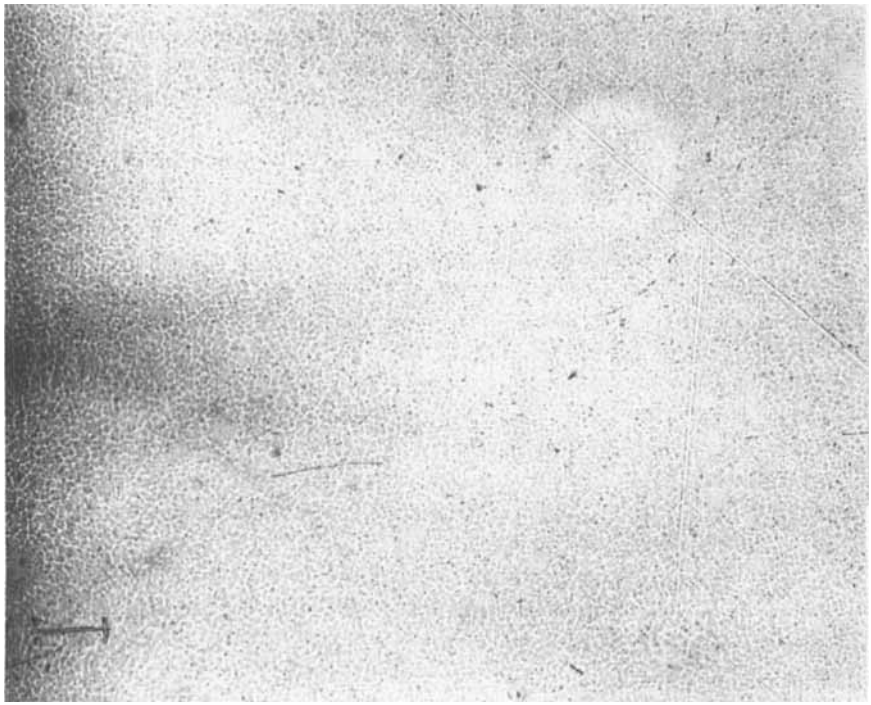


FIG. 1. Micrograph of crosslinked polyester after 8 d at pH 5.4 and 7.4. The bars represent 0.2 mm. (Above) pH 5.4, no void formation after 8 d submersion. (Facing page) pH 7.4, some voids formed after 8 d submersion.

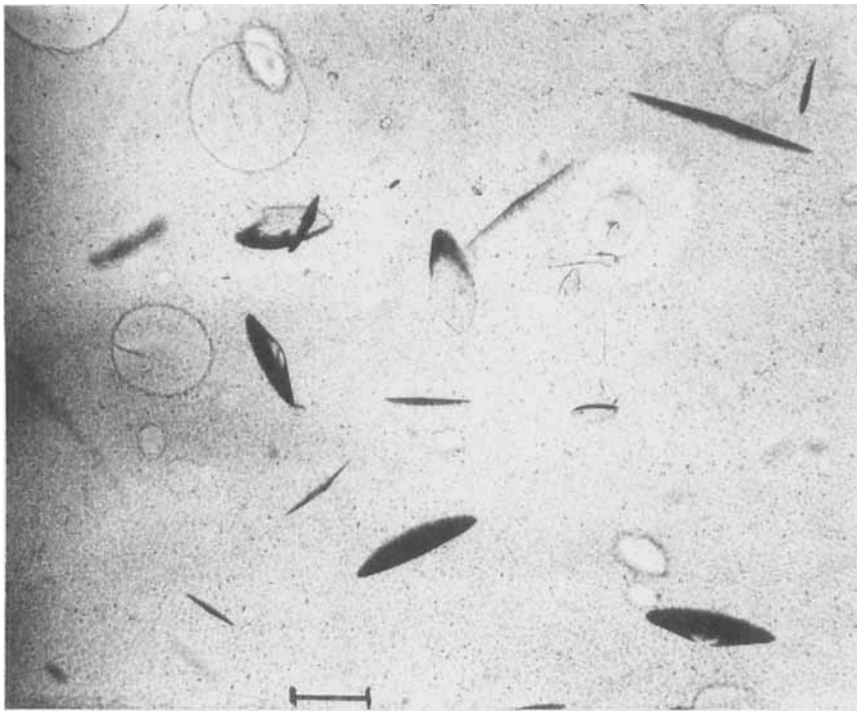


FIG. (continued)

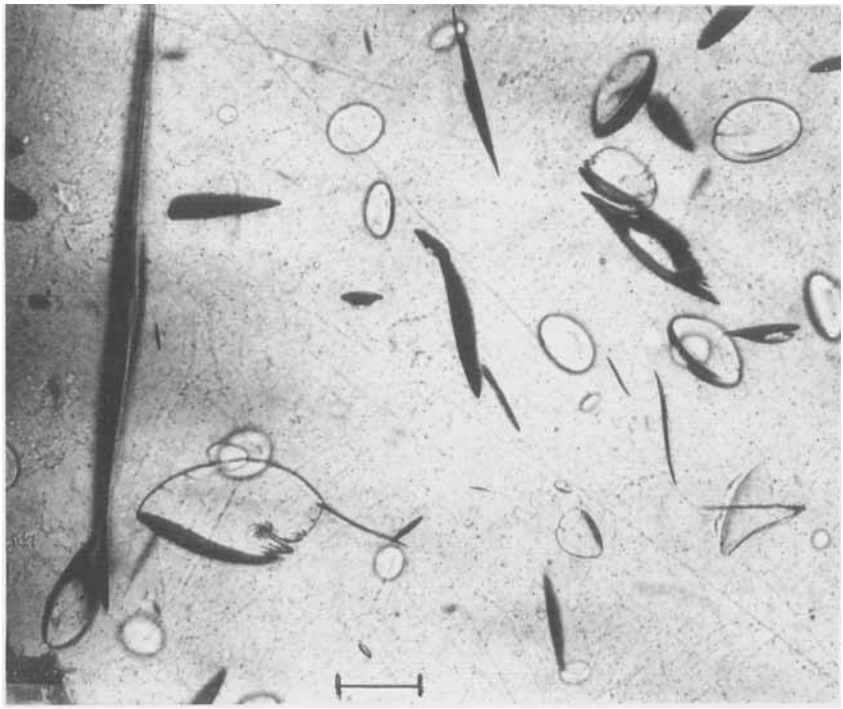


FIG. 2. Micrograph of crosslinked polyester after 8 d at pH 10.0. The bars represent 0.2 mm. (Above) Regular illumination showing voids, 8 d at pH 10.0. (Facing page) Same view under crossed polarizer and analyzer.

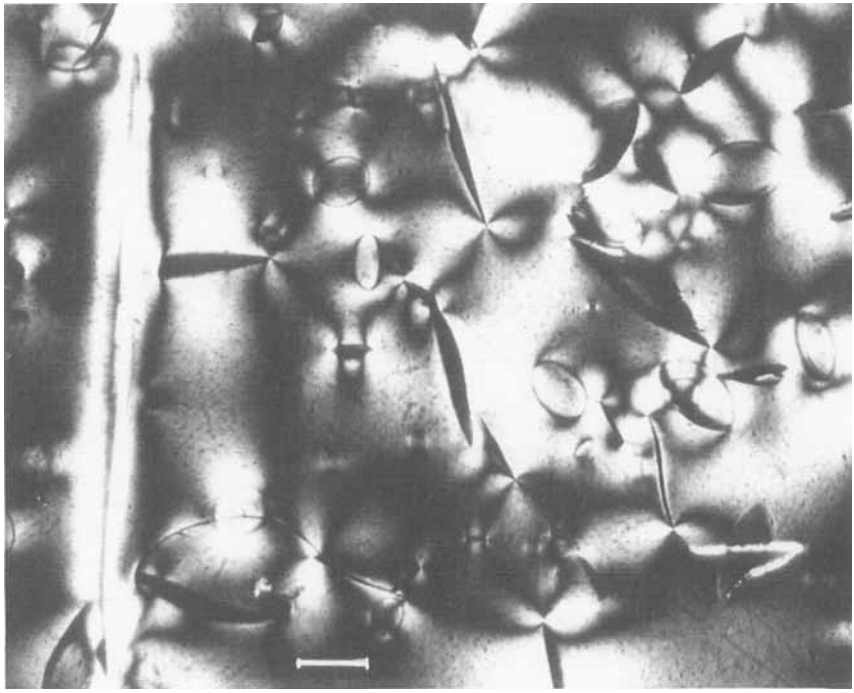


FIG. (continued)

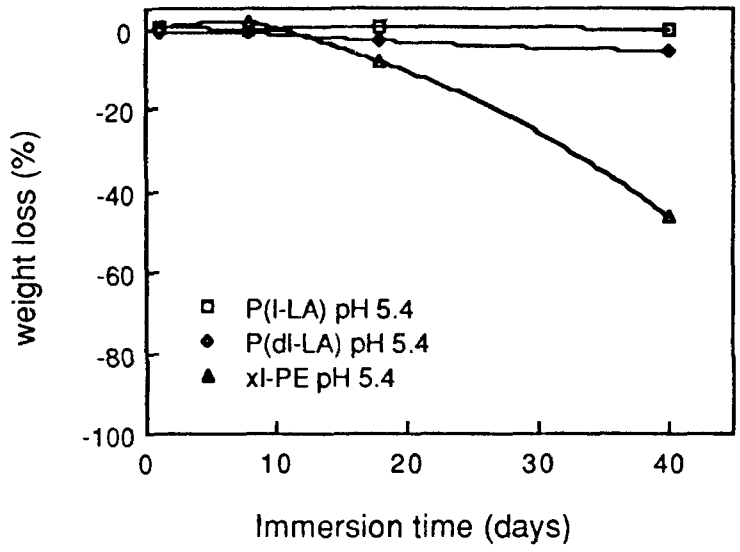


FIG. 3. Change in dry weight during hydrolysis, pH 5.4.

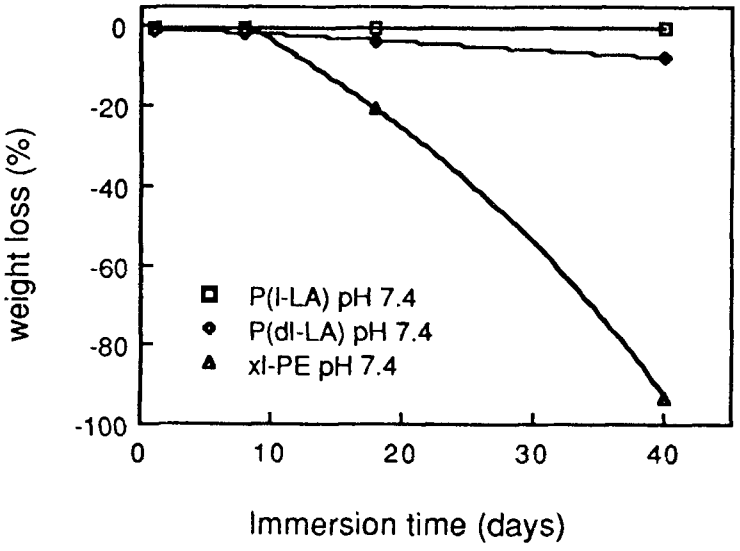


FIG. 4. Change in dry weight during hydrolysis, pH 7.4

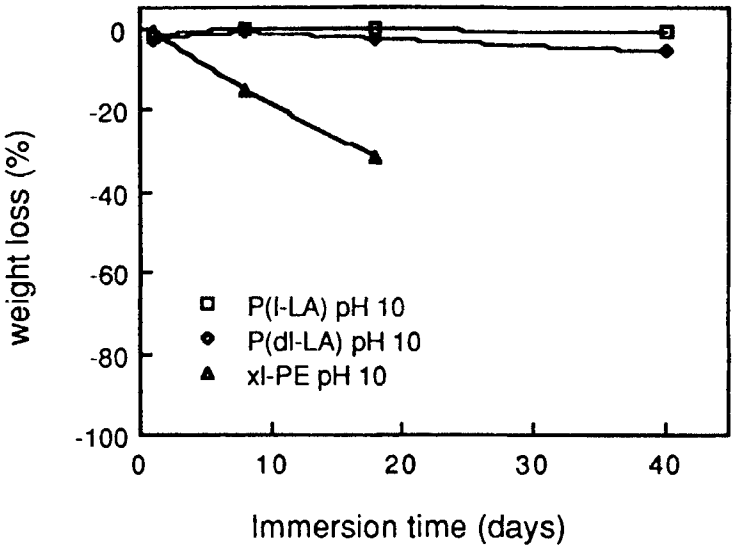


FIG. 5. Change in dry weight during hydrolysis, pH 10.0.

TABLE 5. Hydrolysis Data[a]

	pH 5.4			pH 7.4			pH 10.0		
Day	kl	ll	xl	dl	ll	xl	dl	ll	xl
1	-1.2	0.3	0.2	-1.1	-0.2	-0.2	-2.9	-2.0	-0.7
8	-1.0	0.0	1.6	-1.5	-0.4	-0.3	-1.1	0.0	-15.2
18	-3.0	0.4	-8.1	-3.4	-0.4	-20.6	-2.7	-0.4	-31.5
40	-5.5	-0.4	-46.2	-7.9	-0.4	-93.2	-5.6	-0.8	—

[a]Percent weight change (dry). dl = PDLLA. ll = PLLA. xl = crosslinked polyester.

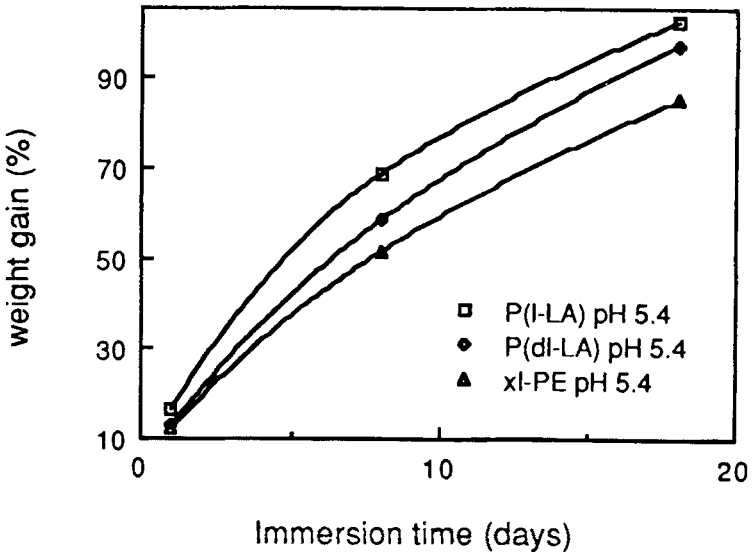


FIG. 6. Change in wet weight during hydrolysis, pH 5.4.

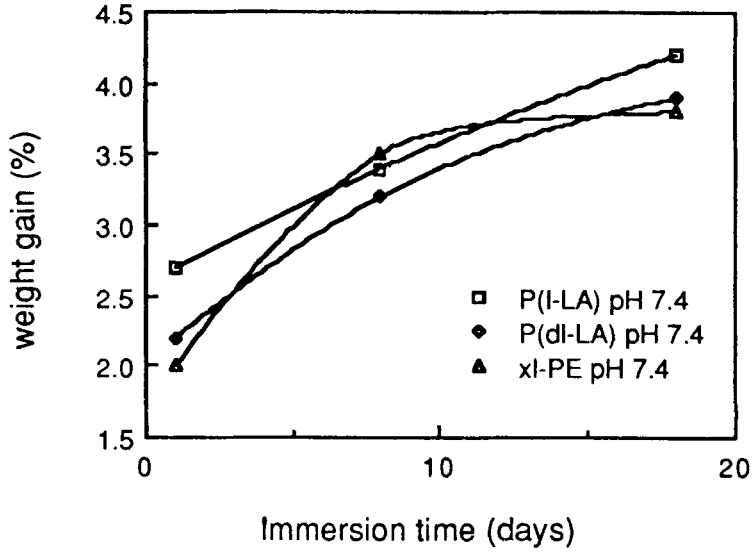


FIG. 7. Change in wet weight during hydrolysis, pH 7.4.

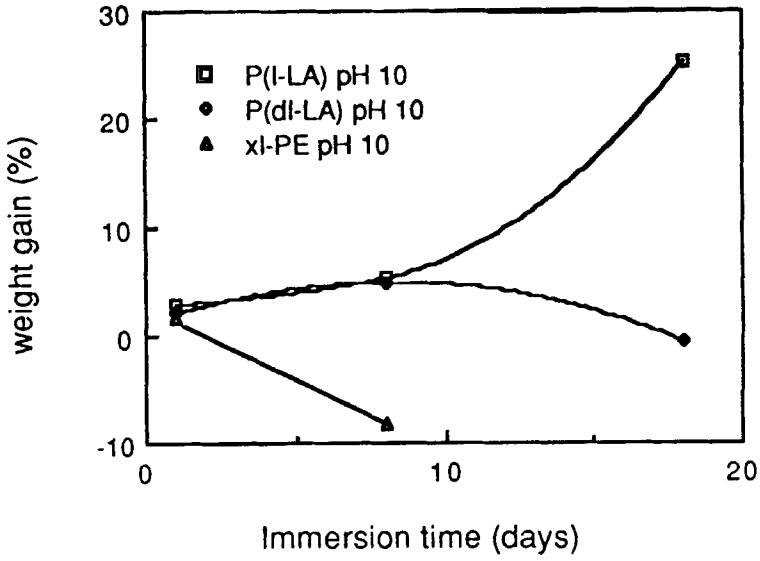


FIG. 8. Change in wet weight during hydrolysis, pH 10.0

TABLE 6. Hydrolysis Data[a]

	pH 5.4			pH 7.4			pH 10.0		
Day	dl	ll	xl	dl	ll	xl	dl	ll	xl
1	12.9	16.3	12.2	2.2	2.7	2.0	2.0	2.8	1.5
8	58.6	68.8	51.6	3.2	3.4	3.5	4.9	5.3	-8.2
18	96.9	102.0	84.8	3.9	4.2	3.8	-0.6	25.3	–

[a]Percent weight change (wet). dl = PDLLA. ll = PLLA. xl = crosslinked polyester.

may be misleading because of simultaneous weight loss and weight gain due to concurrent hydrolysis of soluble fragments and swelling. All materials absorb pH 5.4 buffer solution extensively. Surprisingly, the poly(*L*-lactic acid) sample absorbs the most, followed by poly(*D,L*-lactic acid), with the crosslinked samples absorbing the least. After 18 d the crosslinked samples in pH 10 buffer had disintegrated considerably, and wet weights were not recorded.

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