

Hydrolytic Degradation of Nonoriented Poly(β -Propiolactone)

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SYNOPSIS

The hydrolytic degradation of poly(β -propiolactone) with a molecular weight M_w of 32,000 has been studied in a buffered salt solution (pH 7.2) at 37°C. Within 42 days, the embrittlement of the samples made tensile strength measurement impossible, which is due to the rapid reduction of molecular weight, 50% reduction after 49 days. The maximum weight due to water absorption was measured to 1.2 wt %, reached after 2 days. The absorbed water acts as a plasticizer in poly(β -propiolactone) observed by the displacement in the maxima of the $\tan \delta_\alpha$ peak. A fast increase of crystallinity in the samples has been observed during the first 50 days of degradation, with the increase continued up until 190 days, after which a decline of the crystallinity can be observed, indicating hydrolytic degradation of the crystalline part of the samples. The mass loss of the samples becomes prominent after 150 days of immersion and reached a value of 14.6% after 260 days.

INTRODUCTION

The degradation of polymers has for many years been considered to be an unwanted process, but today we seek tailor-made degradable materials that can be utilized in medical and agricultural applications and also as disposable packages. Great interest has arisen for this type of material together with a need for testing their usefulness, and this has led to a high activity directed toward creating and characterizing such new materials in various medical applications.^{1,2} The most successful class of polymers, where degradability is one of the prior demands, has undoubtedly shown to be the aliphatic polyesters.

The hydrolytic degradation of the polymers derived from α -hydroxy acids such as poly(glycolic acid) or poly(lactic acid) have been studied in a number of articles, whereas polymers from β -hydroxy acids have received less attention with the exception of poly(β -hydroxybutyrate).

In a previous paper,³ we discussed the hydrolytic degradation of oriented poly(β -propiolactone)

(PPL) and have reported that the tensile strength was not measurable after a period of 240 days; yet, in spite of the fact that they had been stored for 1 year in a buffered salt solution, no changes in their appearance or shape could be seen. This emphasizes the very important question of whether the structure of PPL allows a total degradation, i.e., even from the crystalline phase.⁴

The present work focuses on the degradation of nonoriented strips of PPL in terms of change in crystallinity, decrease in molecular weight, and loss of weight. In this paper, we also discuss how the water absorption influences the position of the $\tan \delta_\alpha$ peak of the polymer.

EXPERIMENTAL

β -Propiolactone (β -PL)

β -Propiolactone was synthesized from ketene, which was obtained by pyrolysis of acetone over a nichrome wire,⁵ and gaseous formaldehyde, which was produced from a slurry of paraformaldehyde in silicone oil. These two gases were passed through an ethyl acetate solution maintained at 15°C, containing 2% by volume of a catalyst solution that was prepared

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by mixing a solution of 20 g AlCl_3 of 50 g of acetone with a solution of 1.5 g ZnCl_2 in 10 g acetone.⁶ The yield of β -PL was very low, and this may be due to the difficulty in obtaining an equimolar gas flow into the system. The β -PL was distilled with reduced pressure to remove the catalyst residues. Before polymerization, the β -PL was dried over anhydrous sodium sulphate for 3 days at 4°C, rapidly passed through two columns containing anhydrous calcium chloride, and then immediately distilled under reduced pressure (32°C, 1.5 mbar).

Polymerization

An empty three-necked round-bottomed flask was maintained at 200°C overnight and then removed from the oven and immediately sealed with rubber septum. The flask was allowed to cool at room temperature while a stream of dry N_2 was passed through it. β -Propiolactone 100 g (1.4 mol) and pyridine 120 μL (1.5 mmol) were introduced by means of a syringe.

The flask was then placed in a water bath at 5°C, controlled by a thermostat, and dry N_2 was passed through it during the time of polymerization, which lasted for 11 days. The polymer was dissolved in 1 L of chloroform and precipitated in 6 L of methanol. Drying to constant weight gave a yield of 94%. The polymer was stored under dry N_2 atmosphere.

Preparation of the Films

Seven grams of the precipitated and dried polymer was slowly compressed between two Mylar foils at room temperature and maintained under pressure, 200 kg/cm², overnight. The sample was then melt pressed at 100°C for 10 min at the same pressure and was allowed to cool down at room temperature under pressure, 50 kg/cm². Strips of 50 × 6 mm having a nominal thickness of 0.5 mm were cut.

Degradation and Sample Handling

After being weighed, each strip was placed in bottles that contained 20 mL buffered salt solution⁷ having a pH of 7.2. The bottles were placed in a shaking chamber maintained at 37°C. Prior to testing, five bottles were removed, the strips were rinsed for a short time under running water (deionized), and the surface was then dried with a soft tissue. The "wet" mass of the samples was determined. Two samples were used for reflection IR, SEM, DMTA, and tensile measurements. The other three were vacuum dried at 0.2 mbar and 23°C for 5 days. Their

"dry" mass was measured prior to DSC and molecular weight determinations.

Instrumentation

All IR spectra were recorded using a Perkin-Elmer FTIR model 1710 spectrometer equipped with a 3600 data station. The reflection spectra were obtained using a Spectra Tech 4X beam condenser with a micro ATR and a KRS-5 crystal.

The melting endotherm of the polymer was monitored on a Perkin-Elmer DSC-2 at a heating rate of 10 K/min. The fraction of crystallinity was calculated using the standard heat of fusion for 100% crystalline PPL, $\Delta H^\circ = 30.18 \text{ cal/g}$.⁸ In the case of the thermal glass transition, the polymer was cooled at a rate of 40 K/min and then heated at a rate of 20 K/min. The instrument was calibrated against cyclohexane for low-temperature experiments and against indium for high-temperature experiments.

Inherent viscosity measurements in chloroform were made using a Ubbelodhe viscometer at 30°C. The molecular weight was calculated using the constants, $K = 2.59 \times 10^{-4}$ and $a = 0.72$, in the Mark-Houwink equation.⁹

The dynamic mechanical properties of the samples were determined using a dynamic mechanical thermal analyzer (DMTA) from Polymer Laboratories. The sample was cooled at an approximate rate of 5°C/min and then heated at a constant rate of 1°C/min from -70 to 70°C, and data were recorded for five different frequencies. The specimen was clamped using a small frame with free sample length of 5 mm in the dual cantilever mode.

An ISI Super Mini Sem was used to study the surface on the samples during the degradation. The samples were palladium sputtered 10 × 15 min at 700 V in order not to destroy the sample.

RESULTS AND DISCUSSION

In Figure 1(d), the DSC thermogram for PPL strips reveals a small and broad shoulder just before the melting point, $T_{m(\text{peak})} = 86^\circ\text{C}$. This shoulder is assumed to arise from segregation of more low molecular weight material during the cooling of the samples. The relatively high fraction of crystallinity (60%) naturally depends on the method of preparation; if the sample is cooled from the melt at a rate of 10 K/min and remelted, no segregation can be seen [Fig. 1(e)] and the fraction of crystallinity has decreased to 44%. In the same figure [Fig. 1(a)] we can see that the polymer has a thermal glass

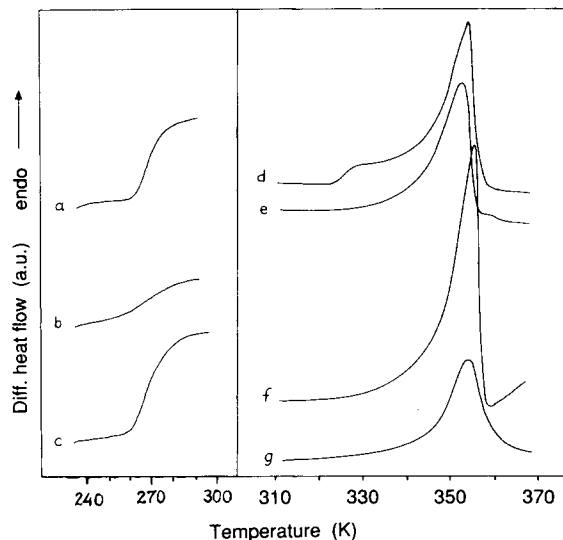


Figure 1 DSC scans of poly(β -propiolactone) samples. The glass transitions of the samples are shown in (a), (b), and (c) and obtained by using a cool rate of 40 K/min and a heat rate of 20 K/min. (a) shows the initial sample cooled from room temperature, (b) is obtained after 190 days of degradation, sample cooled from room temperature, (c) sample in (b) after cooling from the melt. The melting endotherms of the samples are shown in (d), (e), (f), and (g) using a heat rate of 10 K/min and a cool rate of 10 K/min. (d) shows the melting endotherm typical for the initial sample; (e) sample in (d) after one melting and cooling cycle; (f) sample after 190 days of degradation; (g) sample in (f) after one melting and cooling cycle.

transition temperature (T_g) of -4°C . Prior to the measurement of T_g , the sample was dried 5 days under vacuum, 0.2 mbar, for 5 days, which may be the reason for this high value compared to the earlier reported value of -15°C .¹⁰

The strips showed excellent ductile properties, and they could be extended about five to six times their original length in spite of their relatively low molecular weight of 32,000. The tensile measurements gave an initial Young modulus of 1.59 GPa and a tensile strength of >103 MPa (the area used to calculate σ_b is the nonloaded area). The dynamic measurements shown in Figure 2 reveal a lower value at $-8^\circ\text{C} = 0.76$ GPa, at 23°C , and also two transition zones. The major zone at -8°C (1 Hz) is related to the glass transition, whereas the minor zone at 50°C , associated with a small decline in the modulus, is assumed to be due to the melting of the segregated crystalline phase, which according to DSC measurements starts at this temperature [see Fig. 1(d)].

The differences in modulus between the tensile tests and dynamic mechanical measurement is ex-

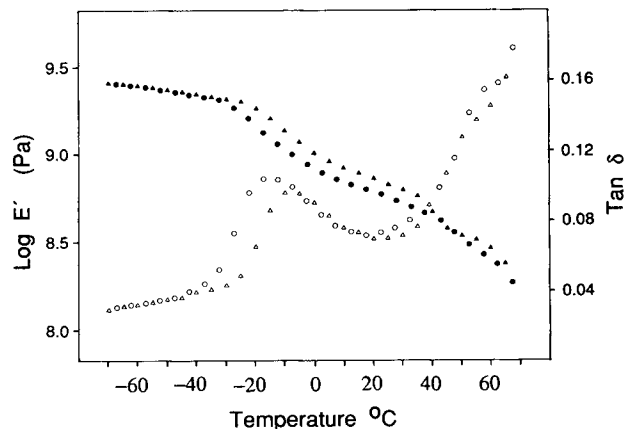


Figure 2 Dynamic storage modulus E' (filled symbols) and $\tan \delta_\alpha$ (open symbols) plotted against temperature for the laminae of the initial sample (\blacktriangle) and the sample after 2 days in the buffer solution (\bullet).

pected because of the difference in type of loading and in “equipment constants.” DMTA is an excellent method of studying how plasticizers, in this case water, affect $\tan \delta_\alpha$. The specimens that were immersed in a buffered salt solution (2 days) showed a displacement of $\tan \delta_\alpha$ by -5.5°C and also a broader peak than the original ones (see Fig. 2).

These measurements were performed during the first 60 days of degradation, and no additional changes (in, e.g., bending modulus, other transitions, appearance, or shape) could be detected except for a further displacement of $\tan \delta_\alpha$ (see Fig. 3). In the same figure, we can see how the $\tan \delta_\alpha$ is affected by the rate of displacement in the dynamic bending experiment. From these data, the activation energy can be calculated to 292 kJ/mol by using the rela-

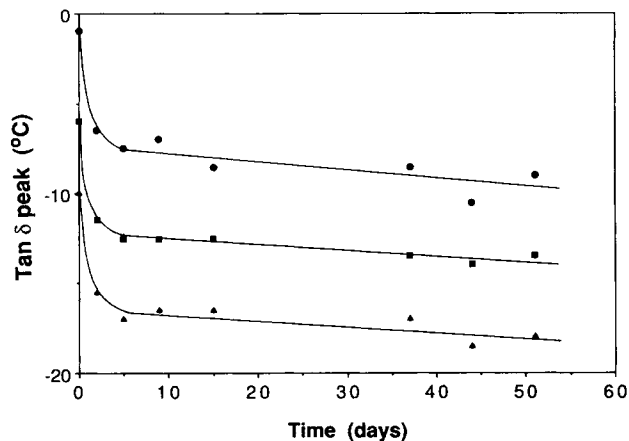


Figure 3 Displacement in temperature of the $\tan \delta_\alpha$ peak of poly(β -propiolactone) plotted against time of immersion in the buffer solution at 0.3 Hz (\blacktriangle), 3 Hz (\blacksquare), and 30 Hz (\bullet).

relationship $\log F = A \cdot \exp(-Ea/RT)$. No significant changes in the activation energy could be seen during the degradation experiment.

The tensile measurements were limited to 37 days because of the embrittlement of the samples, and the last recorded data gave $\sigma_b = 27$ MPa and $E = 1.34$ GPa. There is some uncertainty in the tensile measurements caused by the geometry of the samples and the few samples that were tested. The tensile test does, however, give us a good indication about the time scale for the deterioration of the mechanical properties in the material. The rapid loss of ductile properties is consistent with the large decrease in molecular weight, approximately 50% after 50 days. The same tendency has been reported for poly(L-lactide).¹¹

In Figure 4, the change in weight, expressed as a percentage, is plotted against time. The initial water absorption was completed within 2 days and reached a value of 1.2%. In the first period of degradation, the "wet" weight of the specimens was constant, whereas the "dry" weight, samples dried in vacuum (0.021 mbar, 23°C) for 5 days, started to decline after 9 days. The weight loss is assumed to be due to the leaching out of low molecular weight compounds into the water phase, although it continues at a constant rate up to 120 days. Thereafter, a more rapid mass loss can be observed, indicating that the degradation has advanced to such a point that the degradation products might be able to leave the sample by diffusion. By distinguishing between "wet" and "dry" mass loss, it is possible to study the increase in water absorption caused by degradation. The "dry" and "wet" weights have decreased by 1% and 0.4%, respectively, over this period of 120 days. The difference between the weights shows

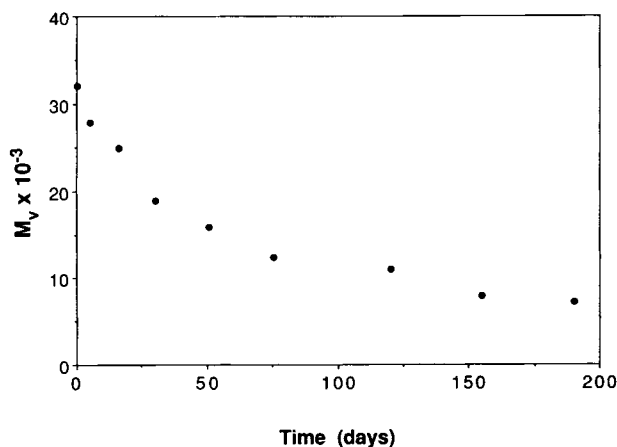


Figure 4 Viscosity average molecular weight of the nonoriented poly(β -propiolactone) as a function of degradation time.

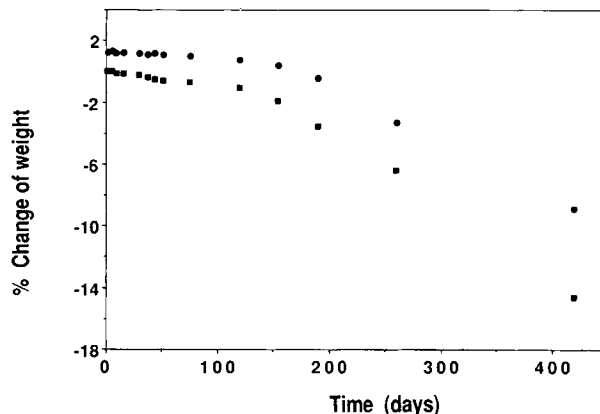


Figure 5 Weight loss of the melt pressed strips as a function of degradation time. The "wet" weight (●) is measured on the surface-dried samples, whereas the "dry" weight (■) is obtained after dehydration of the sample at 23°C and 0.02 mbar for 5 days.

that most of the material leached from the sample is replaced by water. The water uptake based on the dry weight of the sample increases during the degradation¹² as expected, because the environment within the sample becomes more and more hydrophilic (i.e., hydrolysis of ester bonds).

This additional water uptake of 0.5% between 2 and 60 days, together with the increased number of new chain ends, is assumed to be the cause of the constant displacement of $\tan \delta_\alpha$ peak toward lower temperatures during the period from 5 to 60 days in solution (see Fig. 3).

The accelerated weight loss causes the pH of the buffered solution to drop from 7.2 to 5.3 during the interval from 155 to 250 days. The release of degradation products, containing acid groups, will in time exceed the buffer capacity,¹³ and we can therefore expect an accelerated degradation to occur from this time on, due to proton-catalyzed hydrolysis of ester bonds.¹⁴

In Figure 5, we can see that the fraction of crystalline material is slowly increasing during the first period of 190 days of the experiment. The question is whether this increase is caused by a growth in the crystalline phase. If we assume that the mass loss of the specimens, shown in Figure 5, originates from the amorphous phase and calculate the effect of this loss, based on the original fraction of crystalline phase, we can see, in Figure 6, that this cannot be responsible for the total increase. This means that a further crystal growth is taking place within the specimen. The largest increase can be seen at the beginning, presumably caused by an annealinglike effect caused by the environment (37°C and plasticization by water).¹⁵ The fraction of crystalline

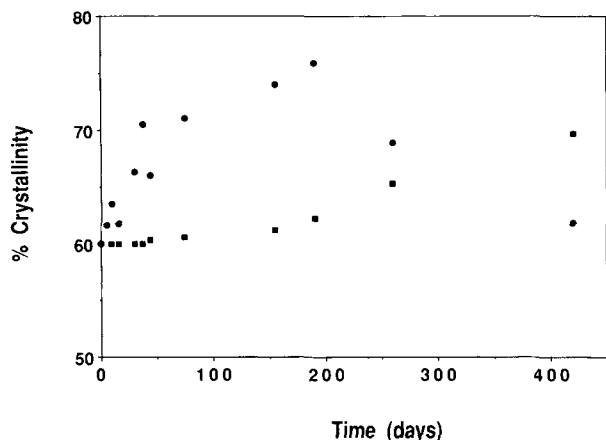


Figure 6 The measured change in the crystallinity during the degradation of poly(β -propiolactone) (●) and the calculated change in crystallinity due to the weight loss from the amorphous phase of the samples (■), based on the initial crystallinity of 60%.

phase continues to increase up to 190 days, after which it starts to decline. Obviously, the hydrolytic degradation of PPL also occurs in the crystalline domains but can first be noticed after some time because the rate of crystallization due to annealing and newly formed chain ends are faster than is the deterioration caused by hydrolytic degradation. In Figure 1(f), the shape of the melting endotherm (sample after 190 days in solution) has become narrower and the melting point (peak value) has increased, indicating a more perfect crystal order compared to the virgin sample in Figure 1(d). The T_g (of dried sample) measured by DSC remains the same during the period of degradation. This should support the assumption made earlier that the further displacement of the $\tan \delta_a$ peak after the first 2 days

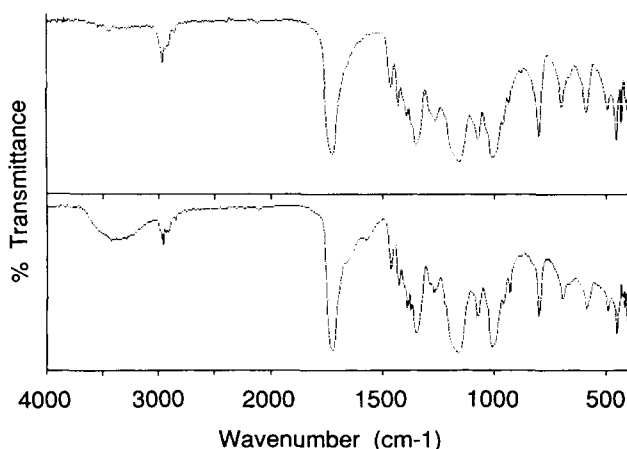


Figure 7 Reflection IR spectra from the surface of poly(β -propiolactone) of the (a) initial surface and (b) surface after 190 days of degradation.

is caused by the additional water uptake and not by the decline in molecular weight (the viscosity average weight is 7200 after 190 days) seen in Fig. 6.

The reflection IR spectra, in Figure 7, show two new bands at 1570 and 1640 cm^{-1} , but apart from this, no other significant changes could be observed. These bands were detected after 60 days and slowly increased during the degradation period. We assume that these bands arise from the hydrolysis product of PPL, which can be expected to be salts of carboxyl end groups or 3-hydroxypropionic acid.

Two important events take place in the strips, namely, a degradation in the bulk, proved by a decline in the molecular weight, presented in Figure 4, and a surface erosion that can be seen in SEM pictures. Figure 8(a) and (b) shows the eroded surface after 190 days of immersion. By scraping off a very thin layer of this surface and looking at the particles between crossed polarizers, the particles show birefringence, yet we have no proof that what

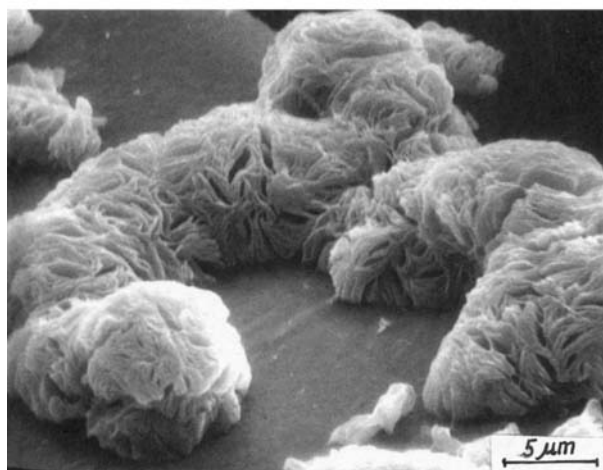
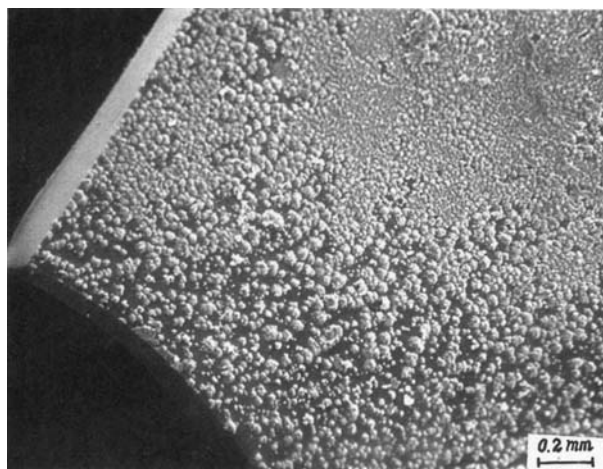


Figure 8 SEM micrographs of the strips after 190 days in the buffered salt solution.

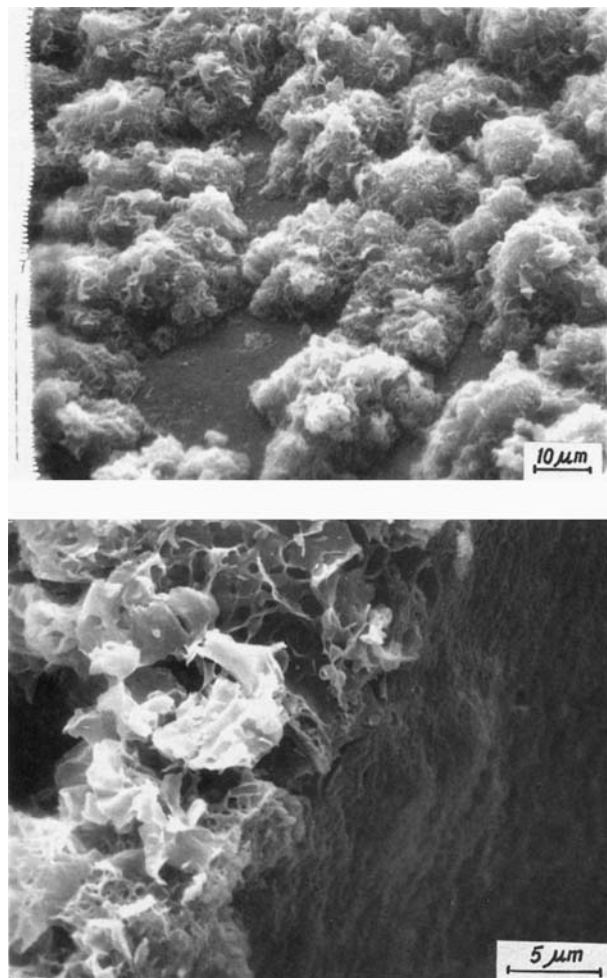


Figure 9 SEM micrographs of the strips after 380 days in the buffered salt solution.

we are seeing are actually partly uncovered spherulites in the PPL sample due to erosion of the amorphous phase. In Figure 9(a) and (b), taken after 380 days of immersion, a more pronounced surface erosion can be seen that gives rise to a very porous shell on the surface. This porous shell is most certainly crystalline, and in Figure 9(b), taken from the edge, we can clearly see that it originates from the bulk of the material.

CONCLUSION

The hydrolytic degradation of melt-pressed PPL strips follows the same pattern as that found in poly(L-lactide) and poly(ϵ -caprolactone). The molecular weight decreases rapidly during the first 50 days. In the same time period, the crystalline phase has a pronounced increase probably due to an an-

nealinglike effect caused by the temperature at which the degradation is performed and the rapid water absorption observed that gives a higher chain mobility, observed by the large displacement of $\tan \delta_{\alpha}$.

After 50 days, the degradation can be noticed by a slower change of increase in the fraction of crystalline phase and a slower decrease in the molecular weight. After 200 days, a decline in the crystalline phase is noticed, which shows that the crystal structure of PPL is attacked by water, indicating that nonoriented structures of this polymer will degrade completely into water-soluble products. The mass loss, however, indicates that the resorption time of this polymer is very long.

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