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J. E. Guillet^a; H. X. Huber^a; J. A. Scott^a

^a Department of Chemistry, University of Toronto, Toronto, Ontario, Canada

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SYNTHESIS AND APPLICATIONS OF PHOTODEGRADABLE POLY(ETHYLENE TEREPHTHALATE)

J. E. GUILLET,* H. X. HUBER, and J. A. SCOTT

Department of Chemistry
University of Toronto
Toronto, Ontario M5S 1A1, Canada

ABSTRACT

A novel synthetic route for the preparation of photodegradable poly(ethylene terephthalate) is described, along with procedures for the synthesis of ^{14}C -labeled plastic. Studies of the labeled plastic in burial tests in active soil show that significant levels of biodegradation are achieved over a 2 to 3 year period for both photodegraded and virgin resin. Computer modeling studies are used to assess the desirability and energy cost of various disposal strategies.

INTRODUCTION

Although the merits of “degradable plastics” as a means of solving some of the problems associated with the disposal of packaging materials in the solid waste stream remain to be demonstrated conclusively, their effective use in litter control is now well established. One of the most successful examples is the Hi-Cone beverage carrier, a rectangular sheet of ca. 15 mil polyethylene into which are punched six holes the size of conventional metal beverage containers. Weighing only a few grams, the manufacture of these packages makes few demands on our “nonrenewable” resources, and they replace plastic and paper carriers which are much more demanding in their resource and energy content. This minimalist design is a triumph of the concept of “under packaging.”

For nearly a decade, a number of United States states, including California, have required this package to be photodegradable because it is highly litter-prone. It also was shown to endanger the lives of birds who often became entangled in the rings. After a number of years of development, an ethylene copolymer containing ca. 1% carbon monoxide was selected to manufacture the degradable variety of the plastic carrier. The resin is now available from two major plastics producers in the United States, and it is estimated that the total volume now exceeds 100 million pounds per annum for this one application. Furthermore, beach and other surveys of plastic litter show at least a tenfold reduction in the number of these carriers observed. In my own personal surveys of California beaches, the senior author can report that he has never seen one of these carriers since the legislation was passed. This confirms the predictions of the computer models we published more than 20 years ago [1]. The photochemistry of ethylene-CO copolymers was studied by Hartley and Guillet at the University of Toronto and published in the first issue of *Macromolecules* [2]. Its use in packaging had been patented by another former employee of Tennessee Eastman a few years earlier. Ethylene can be readily copolymerized with carbon monoxide by the high-pressure free-radical process. Compositions containing about 1% will photodegrade after about 3 weeks of exposure to outdoor sunlight and break up into small particles which are believed to biodegrade completely after photodegradation. At present no other photodegradable plastic can match the ethylene-CO copolymer on a cost/performance basis for this application.

The success of this product in reducing litter suggests the need for other types of photodegradable plastics for the manufacture of highly litter-prone packages, such as the Hi-Cone carriers and beverage containers. An obvious candidate would be photodegradable poly(ethylene terephthalate) (PET). PET can be made photodegradable by copolymerization with glycols or diacids containing ketone groups [3, 4]. Furthermore, masterbatches containing the ketone group can be prepared cheaply from recycled PET via a recently patented process [5] which is described in the Experimental Section. One possible application could be the Hi-Cone carrier, because a 3-mil film of PET would have the necessary physical strength to replace a 15-mil PE-CO, with considerable savings in material and energy costs.

Resource Implications

Both polyethylene and PET can be prepared from renewable resources such as corn or wheat. In fact, for a number of years, all of the world's polyethylene was synthesized from ethyl alcohol produced by fermentation of wheat or other cereals. The ethyl alcohol so produced was dehydrated to ethylene which was subsequently polymerized under high pressure to give polyethylene. Similarly, the chemical intermediates required to make PET could be synthesized from simple organic compounds available from natural products, but at much higher cost. However, the use of wheat or corn as a raw material for the production of plastics would require huge areas of land to be withdrawn from food production, a prospect that could not be morally defended in a world where population pressures have led to widespread starvation [1, 6].

Both PET and PE show accelerated rates of biodegradation after being subjected to extensive photodegradation prior to soil burial in an active environment.

EXPERIMENTAL

Preparation of Ecolyte PET Masterbatch

Photodegradable poly(ethylene terephthalate) (PET) was synthesized by the insertion of the di(ethylene glycol) ester of 4-ketopimelic acid (DGKP) into PET using a reactive extrusion process [5]. A Betol BTS 40 twin screw extruder, with contrarotating screws (40 mm diameter) and 21:1 L/D ratio, was used to conduct the insertion reaction of DGKP into molten PET.

The PET resin (Kodapak PET 9663 clear) was predried overnight and mixed with antimony trioxide (0.04 wt%) and dimethyl terephthalate (2.25 wt%). The mixture was loaded into an AccuRate feeder with the feed rate set at 1 kg/h. The temperature of the extruder barrel was kept in the 220–260°C range.

DGKP was fed into the PET melt stream through a vent port at a rate controlled to yield a 3-wt% addition level. The extruded filament was cooled in a water trough and pelletized.

The reaction product was thermally pressed into clear films and irradiated in a QUV Accelerated Weather Tester. The films failed at 95 hours whereas the control PET resin film remained intact.

Preparation of ^{14}C -Labeled Linear Polyethylene Masterbatch

The synthesis was carried out by the Ziegler process using a Parr pressure reaction apparatus, in hexane using titanium(IV) chloride and triethylaluminum as catalyst.

An ampule of ethylene- ^{14}C with an activity of 1 mCi was broken down by a standard vacuum technique into five bulbs containing 160 μCi each and one bulb with 200 μCi .

Ethylene ^{14}C was obtained from American Radiolabeled Chemicals, St. Louis, Missouri. Reagent-grade hexane (Caledon) was refluxed over metallic sodium under nitrogen. Titanium(IV) chloride (1.0 M solution in dichloromethane) and triethylaluminum (1.0 M solution in hexane) were obtained from Aldrich. Ethylene gas was from Matheson.

The pressure tank on the Parr pressure reactor was repeatedly flushed with ethylene gas to remove all traces of air. A double-valved bulb containing 160 μCi ethylene- ^{14}C was then connected between the ethylene cylinder and the Parr reactor, and the active ethylene was flushed into the pressure tank with ethylene gas. The bulb was then removed and the cylinder was connected directly to the pressure tank. The pressure was increased to 85 lb for the experiment.

The reaction vessel was loaded with 250 mL dry hexane. Titanium(IV) chloride solution (1.74 mL) and 2.9 mL of the triethylaluminum solution were added under nitrogen (0.2% of each catalysts, based on the hexane).

After reattaching the reaction vessel to the Parr pressure apparatus, the shaking mechanism was activated and the valve to the pressure tank was opened to keep the pressure in the reaction vessel at 40 to 45 lb. After 30 minutes the pressure in the tank dropped below 40 lb and the valve was opened completely. At this point the reaction had slowed considerably. After another 30 minutes no further pressure drop could be observed and the reaction was terminated. Any residual catalyst was destroyed with a mixture of propyl alcohol and methanol. The white, fibrous prod-

uct was filtered and washed thoroughly with methanol and then dried in a vacuum oven at 60°C. The yield was 20.3 g.

The activity calculated from the amount of ethylene used (pressure drop from 85 to 23 lb = 62 lb or 73%) was 117 μCi for 20.3 g, or 5.75 μCi per gram. The activity found by scintillation counting was 5.92 μCi by combustion and 5.82 μCi by digestion. The product was stored under N_2 in brown glass bottles.

Experiments using this labeled PE in accelerated biodegradation tests using sewage sludge have been reported previously [7].

Synthesis of ^{14}C -Labeled PET

An ampule of ethylene glycol-1,2- ^{14}C (Sigma) with an activity of 100 μCi was diluted to 10 mL with ethylene glycol (Fisher certified). This solution (1.0 mL) was mixed further with more ethylene glycol to a weight of 17.9 g (the amount calculated for this experiment) with a total activity of 10 μCi .

Step 1. Transesterification. The reaction was carried out in a 250-mL glass vessel equipped with a stainless steel stirrer, a high vacuum stirrer sleeve, a nitrogen inlet, and a take-off adapter. Dimethyl terephthalate (25.0 g, Aldrich 99+%), 8.0 mg magnesium acetate, and 13.2 mg Sb_2O_3 were introduced into the reaction vessel and heated while stirring at 60 rpm in an electric oven under nitrogen to 220°C. After generation and removal of methanol during 2.5 hours, 3.0 mg H_2PO_3 was added to deactivate the catalyst, and the temperature was raised to 250°C for 20 minutes. The resulting bis-hydroxyethyl terephthalate was allowed to cool to room temperature under nitrogen and was left overnight.

Step 2. Polycondensation. The condenser used in the removal of methanol in Step 1 was replaced by traps and the system was connected to a mechanical pump. After reducing the pressure to 0.35 mmHg, the reaction vessel was heated slowly to 280°C while stirring at 60 rpm. The distilling ethylene glycol was collected in an ice-water cooled trap. The second trap was cooled by liquid nitrogen. Initially the pressure increased to 0.56 mmHg, but it gradually decreased as the amount of free ethylene glycol decreased. During the reaction the stirrer power was gradually increased to maintain the speed. After 5 hours the reaction product was so viscous that stirring, even at full power, was no longer possible and heating was stopped. After cooling to room temperature, the product formed an extremely hard mass which stuck tightly to the stirrer and wall of the reaction vessel; it could not be removed by mechanical means. The product was dissolved in a 75:25 mixture of dichloromethane and trifluoroacetic acid, using a total of 250 mL of the solvent mixture. In order to retrieve the product (PET), thin films were cast from the solution and air dried, followed by vacuum drying at 60°C.

A total of 18.0 g PET was recovered, which represents a yield of 53%. The flexible films were stored in a brown glass bottle to protect them from exposure to light. The theoretical activity of 14.5 g, or 42.6% yield, is 4.26 μCi .

Samples for the biodegradation studies were prepared by solution blending 1.0 g of the ^{14}C -labeled PET (0.28 μCi) with 7.0 g of commercial PET (Hoechst) and 0.8 g PET containing 3.8% ketopimelate (Ecolyte PET masterbatch) in 100 mL of a 75:25 mixture of dichloromethane and trifluoroacetic acid. Thin films were pre-

pared from this solution blend. They were air dried, followed by vacuum drying at 60°C. The average thickness of the films was 0.2 mm.

The films were separated into two lots: Lot #1 was stored in a brown glass bottle, and Lot #2 was exposed to the full output of a 275-W GE solar lamp. Lot #2 was placed directly under the source at a distance of 6 inches. After 30 hours the Lot #2 films were extremely brittle. Each lot was then milled in a Scienceware micromill using granulated sugar as a filler to increase the volume of material to the optimum volume required for grinding. The materials were milled for 15 minutes at liquid nitrogen temperature and washed into beakers with distilled water to remove the sugar.

After the sugar dissolved, the PET was filtered off, washed thoroughly, and dried in vacuum at 60°C. The dry powders were screened and passed entirely through a 50-mesh screen. Only traces (1–2%) were smaller than 100 mesh. Total amounts of sample obtained were called Sample A Ecolyte PET (unexposed), 1.27 g, and Sample B exposed for 30 hours at 6.0 inches, 1.50 g.

From each of the above samples, 0.5 g was thoroughly mixed with ca. 1.5 kg of soil mixture and placed in Tanks A and B. The activity of each 0.5-g sample was calculated to be 33 nCi. Actual determination showed 32 nCi, in excellent agreement.

A typical experimental setup is shown in Fig. 1. Three tanks were filled with ca. 1.5 kg of a mixture of unsterilized clay-loam garden soil, peat moss, beach sand, and fine gravel. Polymer samples were mixed into the top 0.5 cm of this mixture: Tank A, soil mixture plus 0.5 g of Sample A; Tank B, soil mixture plus 0.5 g of Sample B; Tank C, soil mixture only for determination of background radiation. Two seedlings each of *Fittonia verschaffeltii* (Hort.:Lem.) Coem., *Pellaea rotundifolia* (G. Forster) Hook., and *Oxalis* sp., were then planted in this mixture and 250 mL of 20% Hoagland's medium [8] was added.

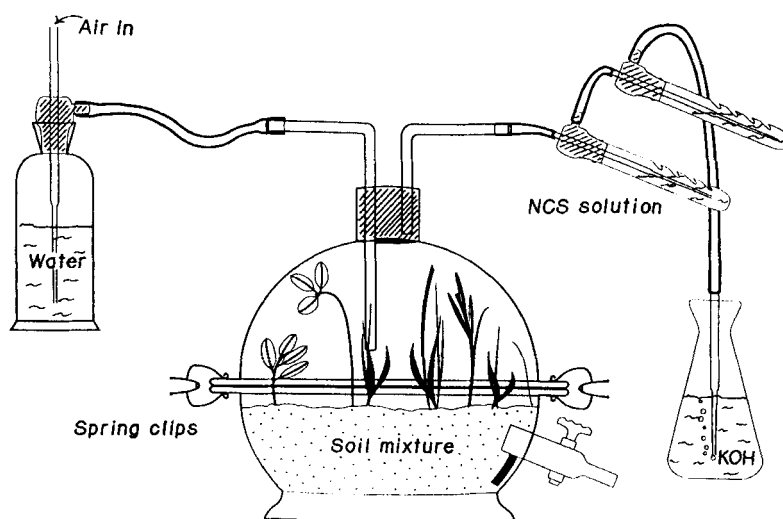


FIG. 1. Terrarium for biodegradation of ^{14}C -labeled polymers.

The tanks were sealed and a constant flow of air was introduced at a rate of 10 mL/min. Exiting gas was bubbled through 1 M KOH to trap carbon dioxide (CO₂). At this rate of airflow, the free volume in each tank was replaced twice daily. Traps were changed every 2 weeks over the course of the experiment.

Short-Term Tests on Biodegradability

Tanks containing soil and labeled plastic samples were prepared. (For details of compositions, see Table 1.)

In the polyethylene experiments, the net accumulative radiation counts (in nCi) for Tanks A1, B1, and C1 are given in Fig. 2. It is clear that photodegradation causes a significant increase in the initial rate of biodegradation as measured by CO₂ evolution. Similar results were shown in the PET experiments (Fig. 3 and Table 2).

In each case the photodegraded plastic shows a more rapid rate of biodegradation than the undegraded material. There is no evidence that the presence of 16% starch in polyethylene causes any acceleration of biodegradation (Fig. 2C). In the case of PET, the unphotolyzed PET does not biodegrade in the first several months, but eventually degrades as rapidly as the photodegraded sample (Figs. 3 and 4).

TABLE 1. Content of Tanks Used in Short-Term Tests

	Soil, dry wt, g	Plant, dry wt, g (final)	Plastic, wt, g	Form
<i>Experiment 1 – Polyethylene</i>				
A1	1472.7	34.1	¹⁴ C-HDPE:LDPE:Ecolyte (20:75:5), 0.5000 g (= 330 nCi)	Powdered
B1	1512.5	21.1	¹⁴ C-HDPE:HDPE (20:80), 0.5000 g (= 375 nCi)	Powdered
C1	1399.3	30.8	¹⁴ C-HDPE:(HDPE + 16% starch) (20:80), 0.5000 g (= 380 nCi)	Film, 1 cm ²
D1	1506.0	26.4	No polymer added	Control
<i>Experiment 2 – Poly(Ethylene Terephthalate)</i>				
A2	1642.4	18.8	¹⁴ C-PET, 0.5000 g (= 33 nCi)	Unexposed, powdered
B2	1559.7	23.6	¹⁴ C-PET, 0.5000 g (= 33 nCi)	Powdered, exposed 30 h at 6 in.
C2	1627.8	23.5	PET, 0.5000 g (= 0 nCi)	Control, unexposed, powdered

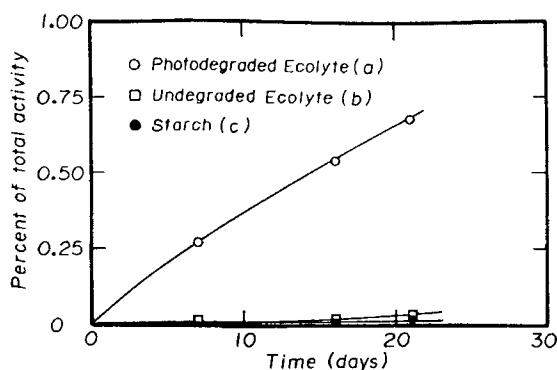


FIG. 2. Biodegradation of polyethylene: accumulative activity of $^{14}\text{CO}_2$.

Long-Term Biodegradation Tests

Harvesting. After about 2 years of plant growth, the tanks were opened, all plant material (including material adhering to the glass or plastic tank) and soil were separated and placed in preweighed, dry aluminum pans. Plant and soil samples were dried to constant weight in a 60°C oven.

Plant Extraction Procedure. Dried plant samples were coarsely crushed and homogenized. Subsamples were taken and further homogenized under liquid nitrogen and redried. Five additional samples of 50 mg from each of the subsamples were combined (individually) with 15.0 mL toluene-based scintillation cocktail (2,5-diphenyloxazole (PPO, 4.0 g, New England Nuclear), 1,4-bis[2-(5-phenyloxazolyl)-benzene] (POPOP, 0.5 g, Beckman), and scintillation grade toluene (1 L,

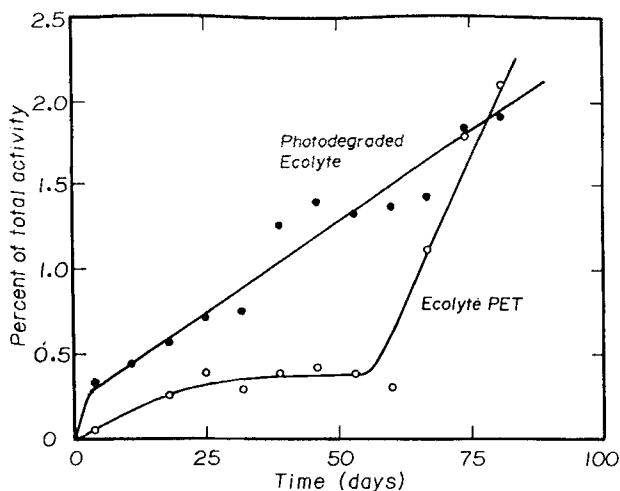


FIG. 3. Net production of carbon dioxide from PET.

TABLE 2. Biodegradation Study of ^{14}C Labeled PET

Days	Tank A (PET)		Tank B (Ecolyte PET) photodegraded	
	nCi ^a	%	nCi ^a	%
4	0.013	0.04	0.104	0.33
11	—	—	0.139	0.43
18	0.078	0.24	0.180	0.56
25	0.122	0.38	0.229	0.72
32	0.090	0.28	0.237	0.74
39	0.121	0.38	0.400	1.25
46	0.131	0.41	0.442	1.38
53	0.119	0.37	0.417	1.30
60	0.094	0.29	0.432	1.35
67	0.352	1.10	0.450	1.41
74	0.565	1.77	0.526	1.54

^aAfter subtraction of counts from control Tank C.

Fisher) in glass scintillation vials. The samples were counted on a Beckman liquid scintillation counter.

Soil Extraction Procedure. Soil (200 g) was added to either 50 mL MeOH or 50 mL 1:1 MeOH:distilled water in 125 mL Erlenmyer flasks. The flasks were sealed, placed on a rotary shaker set at 60 rpm, and extracted for 7 days. Samples were allowed to settle. The supernatant liquid was drained and centrifuged at 15 Krpm for 30 minutes. The supernatant extract was decanted and equally divided

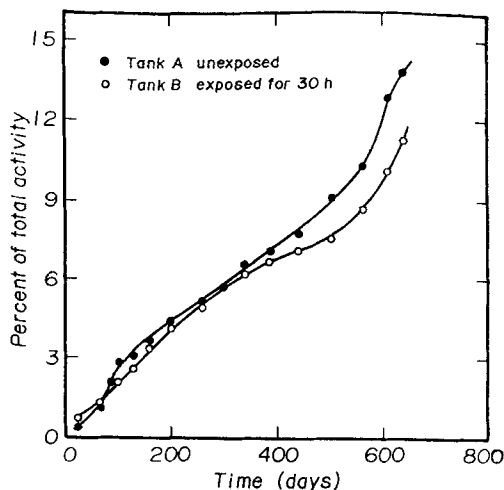


FIG. 4. Biodegradation of PET.

into two glass scintillation vials (10.0 mL to each). The toluene-based scintillation cocktail described above was added to a total volume of 15 mL. The samples were counted on a Beckman liquid scintillation counter.

The long-term release of $^{14}\text{CO}_2$ is shown in Fig. 4. Total release from both photodegraded and undegraded PET is about 15% over 2 years, which compares favorably to many natural polymers. Furthermore, the rate of $^{14}\text{CO}_2$ evolution appears to accelerate as the degradation proceeds, which might be expected to occur as the polymer fragments break down in molecular weight.

Preliminary results on plant and soil assays are shown in Table 3. In the case of PET, plant assays indicate that the plants contain nearly as much ^{14}C as the CO_2 released. A similar result was observed in earlier studies with ^{14}C -labeled Ecolyte PS [9]. Taken together with the CO_2 results, this suggests that PET is more than 30% biodegraded after burial for 2 years in an active soil environment, a result comparable to those reported for straw by Jansson [10].

No appreciable amounts of radiolabeled residues were detected from either 50/50 water/methanol or methanol extraction of PET containing soils, suggesting that most low-molecular weight compounds produced are biodegraded more rapidly than their precursors. However, some methanol-soluble products were extracted from the linear polyethylene tests (Table 3). The composition of these residues will be investigated further.

Environmental Considerations

The long-term burial tests described herein strongly suggest that PET is inherently a truly biodegradable plastic. Furthermore, its return to the environmental carbon cycle when it becomes litter can be accelerated by minor modifications in its chemical structure to include small amounts of ketone carbonyl groups. This procedure can be carried out either in its original synthesis or in a subsequent reactive extrusion to form a masterbatch which can be pellet blended before extrusion to film, or blow molded to provide bottles or other containers.

Aluminum cans have been considered to be environmentally friendly for beverage containers because they are easy to recycle. But the same is true of PET, and

TABLE 3. Results of Long-Term Burial Tests (2 years)

Composition	Morphology	Localization of ^{14}C (%)			
		Soil ^a	Plant	Air (CO_2)	Total %
PET, unexposed	Powder	0	14	15	30
PET, exposed 30 h at 19 cm	Powder	0		14	14
HDPE:LDPE:Ecolyte (20:75:5)	Powder	5			
^{14}C -HDPE:HDPE (20:80)	Powder	10			
HDPE:HDPE containing 16% starch (20:80)	Film, 1 cm ²	0			

^aBased on methanol extraction at 25°C.

TABLE 4. Energy Costs of Beverage Containers^a

Container	MJ/kg	kWh/container
Aluminum can	305	2.4
PET bottle	107	0.84

^aFrom I. Boustead and G. F. Hancock, *Energy and Packaging*, Ellis Horwood Publishers, Chichester, 1981.

its energy cost is much lower. Data on the relative energy costs of a typical aluminum can and a PET 450 mL bottle calculated from the data of Boustead and Hancock [11] are shown in Table 4. The aluminum can requires three times as much energy to manufacture, and if not recycled a similar waste of energy. Most new electrical plants in the United States use fossil fuels (gas, coal, oil) to generate the power for aluminum production, so that in this case the use of aluminum cans causes a much greater drain on nonrenewable resources than do plastic containers. Furthermore, an aluminum can is virtually indestructible in the environment and represents a form of "permanent litter." In view of the billions of such containers produced annually in the developed countries and the relatively low rate of recycling (< 40%), this is a consideration that urgently needs attention.

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