

# Biodegradable Polymers: Photolysis and Fungal Degradation of Poly(arylene Keto Esters)\*

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## Synopsis

Poly(keto esters) were prepared from 4,4'-bis(chloroacetyl) diphenyl ether, 4,4'-bis(bromoacetyl)diphenyl ether, and 4,4'-bis(2-bromopropionyl)-diphenyl ether and aliphatic diacids of 6, 8, 9, 10, and 12 carbon atoms. Low-molecular-weight polymers were found to support the growth of *Aspergillus niger* and *Aspergillus flavus*. Introduction of methyl group to the polymer chain decreased the susceptibility of the polymers to fungal attack. Although monomeric model compounds were found to undergo photodegradation the poly(keto esters) underwent mostly crosslinking when irradiated with UV light.

## INTRODUCTION

There are increasing interests in biodegradable polymers in recent years.<sup>1,2</sup> The ease of disposing biodegradable polymer wastes and the use of biodegradable polymers in controlled release formulations of drugs and agricultural chemicals, and agricultural mulches are some of the incentives behind recent research activities. For uses in the agricultural field, both the biodegradability and the photodegradability of the polymers are important, since the polymers are exposed to various amounts of sunlight in the field.

Results from our studies on biodegradable polymers suggested that the presence of hydrolyzable functional groups and conformational flexibility are among the most important factors affecting the biodegradability of synthetic polymers.<sup>3</sup> Among the polyesters, the aliphatic polyesters have been found to be readily biodegradable.<sup>3-5</sup> Photodegradable polyesters were prepared from aliphatic keto acids.<sup>6</sup> Aliphatic polyesters, as a class, are generally characterized by low melting and poor strength, which limit their applications. Aromatic polyesters, on the other hand, are rigid crystalline materials and are generally found to resist biodegradation.<sup>3,7</sup> Copolymers containing high aromatic contents were also found to resist fungal attack.<sup>2</sup> Esters of aromatic keto acids are hydrolyzable and photodegradable. Sheehan and Umezawa<sup>8</sup> used the *p*-medoxyphenacyl and 2-methylphenacyl groups as photosensitive protecting groups for the carboxylic acid groups of amino acids in peptide synthesis. We reasoned that polymers containing aromatic keto ester groups in the main chains might be photodegradable as well as biodegradable. We report here the synthesis, biodegradation, and photolysis of the polymers containing aromatic keto ester groups.

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## EXPERIMENTAL

Melting points were taken on a Reichert hot-stage melting point apparatus or on a Perkin-Elmer differential scanning calorimeter (DSC-1B) and are uncorrected. Nuclear magnetic resonance spectra were recorded on a Varian EM-360A instrument. Ultraviolet spectra were recorded on a Beckmann DB spectrophotometer. Elemental analyses were performed by Baron Consulting Co. of Orange, CT.

### Reagents

The following chemicals were obtained from Aldrich Chemical Co., Inc., Milwaukee, WI: bromoacetyl bromide, 2-bromopropionyl chloride, chloroacetyl chloride, *m*-cresol, 1,10-decanedicarboxylic acid, diphenyl ether, *N*-methylpyrrolidone, sebacic acid, and suberic acid.

The following chemicals were obtained from Eastman Organic Chemicals, Rochester, NY: adipic acid, azelaic acid, 2-bromopropionyl bromide, and *N*-methylpyrrolidone.

Hexanoic acid and triethylamine were obtained from Matheson, Coleman and Bell, East Rutherford, NJ. Lithium carbonate was purchased from Mallinckrodt Chemical Works, New York. Solvents were purified by recommended procedures prior to use.<sup>9</sup>

Sabourand's and dextrose agar were obtained from Difco, Detroit, MI. *Aspergillus niger* strain ATCC 9642 and *Aspergillus flavus* strain ATCC 9643 were used.

### Syntheses

#### *4,4'*-Bis(chloroacetyl)diphenyl Ether(1)

Methylene chloride, 50 ml, was introduced into a 500-ml round-bottomed flask equipped with a magnetic stirrer, dropping funnel, and calcium chloride drying tube and connected to the aspirator. As vigorous stirring was maintained, 58 g (0.434 mole) anhydrous aluminum chloride and 43.4 g (0.38 mole) chloroacetyl chloride. The mixture was cooled to  $-10^{\circ}\text{C}$  in a sodium chloride ice bath. A solution of 29.45 g (0.173 mole) diphenyl ether in 20 ml methylene chloride was added dropwise over a 30-min period. The mixture was allowed to warm slowly to room temperature and was stirred for a total of 24 hr. The mixture was poured slowly into 200 g ice in the hood. A pale green precipitate formed. Enough methylene chloride was added to dissolve the precipitate and the mixture was transferred to a separatory funnel. The methylene chloride layer was separated and the aqueous layer was extracted with a small amount of methylene chloride. The aqueous layer was discarded and the combined methylene chloride extracts were washed with distilled water until the pH of the water layer was 7. The methylene chloride layer was dried with anhydrous magnesium chloride and evaporated. A good solid remained. Recrystallization three times with decolorizing yielded 32.82 g (58.73%) *4,4'*-bis(chloroacetyl)diphenyl ether (1), melting point  $108-109.5^{\circ}\text{C}$  (lit.  $114^{\circ}\text{C}$ ).<sup>11</sup>

ANAL. Calcd for  $\text{C}_{16}\text{H}_{12}\text{Cl}_2\text{O}_3$ : C, 59.44%; H, 3.72%; Cl, 21.98%. Found: C, 60.01%; H, 3.90%; Cl, 22.30%.

*4,4'-Bis(bromoacetyl)diphenyl Ether (2)*

This compound was prepared as above using 43.42 g (0.326 mole) anhydrous aluminum chloride in 40 ml  $\text{CH}_2\text{Cl}_2$ , 57.53 g bromoacetyl bromide (0.285 mole), and 22.1 g (0.13 mole) diphenyl ether in 15 ml methylene chloride. The yield was 28.19 g (52.69%) cream-colored solid, melting point 117.5–120°C (lit. 13,14 121°C, 124°C).<sup>11,12</sup>

ANAL. Calcd for  $\text{C}_{16}\text{H}_{12}\text{Br}_2\text{O}_3$ : C, 46.60%; H, 2.91%; Br, 38.83%. Found: C, 46.88%; H, 3.80%; Br, 39.20%.

*4,4'-Bis(2-Bromopropionyl)diphenyl Ether (3)*

This compound was prepared in a similar manner using 28.98 g (0.22 mole) anhydrous aluminum chloride 32.57 g (0.19) 2-bromopropionyl chloride in 25 ml methylene chloride and 14.73 g (0.037 mole) diphenyl ether in 10 ml methylene chloride. The yield was 23.79 g (62.44%) pale yellow solid, melting point 106–112°C.

ANAL. Calcd for  $\text{C}_{18}\text{H}_{16}\text{Br}_2\text{O}_3$ : C, 49.09%; H, 3.64%; Br, 36.36%. Found: C, 49.33%; H, 3.79%; Br, 36.79%.

*4,4'-Bis(2-Chloropropionyl)diphenyl Ether (4)*

This compound was prepared as above using 80 g (0.6 mole) anhydrous aluminum chloride, 51.68 g (0.41 mole) 2-chloropropionyl chloride and 34 g (0.2 mole) diphenyl ether. The yield was 18.06 g (25.73%) pale yellow solid, melting point 87.5–92.5°C. Attempts to polymerize this compound were not successful.

ANAL. Calcd for  $\text{C}_{18}\text{H}_{16}\text{Cl}_2\text{O}_3$ : C, 61.54%; H, 4.56%; Cl, 20.23%. Found: C, 61.32%; H, 4.82%; Cl, 19.94%.

*Model Diester (5)*

In a 125-ml Erlenmeyer flask were mixed 6.46 g (0.02 mole) 4,4'-bis(chloroacetyl)diphenyl ether, 4.64 g (0.04 mole) hexanoic acid, and 4.04 g (0.04 mole) triethylamine in 40 ml *N,N*-dimethylformamide. The flask was swirled until all dissolved and was placed in the refrigerator 24 hr. Then the contents were poured into 350 ml iced water with stirring. The white solid was filtered, washed with distilled water, and dried *in vacuo* 48 hr at 50°C. Recrystallization twice from 2-propanol yielded 6.23 g (64.63%), melting point 118.5–120.5°C.

ANAL. Calcd for  $\text{C}_{28}\text{H}_{34}\text{O}_7$ : C, 69.71%; H, 7.05%. Found: C, 69.75%; H, 7.11%.

*Model Diester (6)*

This compound was prepared in a similar manner using 4.40 g (0.01 mole) 4,4'-bis(2-bromopropionyl)diphenyl ether, 2.32 g (0.02 mole) hexanoic acid, and 2.02 g (0.02 mole) triethylamine in 20 ml *N*-methylpyrrolidone. The product was a viscous oil. This material was purified using column chromatography on silica gel. Carbon tetrachloride, methylene chloride and methanol were eluting solvents. The pure material recovered weighed 3.25 g (63.73%).

ANAL. Calcd for  $\text{C}_{30}\text{H}_{38}\text{O}_7$ : C, 70.59%; H, 7.45%. Found: C, 69.75%; H, 7.28%.

*Polymers*

The synthesis of the polymers is summarized in Tables I, II, and III.

*At 0°C*

The diamine and bishaloketones were dissolved in 150 ml of the appropriate solvent and swirled until dissolution occurred. The flasks were stoppered and placed in the refrigerator for 48 hr, with frequent shaking. The slurry which formed was poured into 1:1 iced water with stirring. The precipitate was collected with suction and washed with a large quantity of distilled water and acetone. It was dried *in vacuo* 48 hr at 50°C. The yields and melting temperatures are given in Table I.

*At 80°C*

The reactants were dissolved in 150 ml of the appropriate solvent in a three-necked, round-bottomed flask equipped with a nitrogen inlet and a magnetic stirrer. The flask was heated in an oil bath to 80°C and maintained at that temperature for 18 hr. The flask was cooled under nitrogen and the solution was poured into 1.5:1 iced water with stirring. The pale yellow precipitate was collected with suction, washed with distilled water and acetone, and dried *in vacuo* 48 hr at 50°C. Yields and melting temperatures are given in Tables I, II, and III.

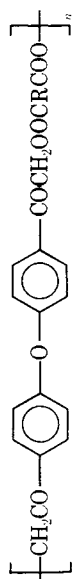
**PHOTOLYSIS STUDIES****Model Compounds**

Model compounds (5) (0.5 g) and (6) (0.63 g) were photolyzed in a 250-ml photochemical reaction vessel from Ace Glass Co., Inc. through Pyrex using a 450-W Hanovia mercury vapor lamp. The compounds were dissolved in dry ethanol and photolyzed under nitrogen for 6 hr. At that time, no starting materials remained. The ethanol was evaporated and the samples were redissolved in ethyl acetate. Extraction with 1*N* potassium carbonate removed the hexanoic acid product. Neutralization with 2*N* HCl and extraction with ether yielded 0.02 g hexanoic acid (16.67%) for model (5) and 0.99 g hexanoic acid (32.14% of the theoretical amount) for model (6). The ethyl acetate layer was evaporated. Column chromatography on the residue using silica gel and 4:1 v/v chloroform:methanol resulted in a mixture. For compound (5), proton NMR in deuterated chloroform indicated that almost all of the mixture was 4,4'-bis(acetyl)diphenyl ether. A very small peak at  $\delta$  5.3 was due to the methylene protons of the ester. A very large peak at  $\delta$  2.6 was due to the methyl group of the ketone product. For (6), proton NMR indicated that about two-thirds the ester links had been converted to ethyl groups. The quartet at  $\delta$  6.0 was due to the methyne hydrogen of the ester and that at  $\delta$  3.0 was due to the methylene hydrogens in 4,4'-bis(propionyl)diphenyl ether.

Samples were submitted for high-resolution mass spectral analysis.

For (5), Calcd for  $C_6H_{12}O_2$  (hexanoic acid): 116.0837; obsd mass: 116.0831. Calcd for  $C_{22}H_{24}O_5$  (monoester): 368.1621; obsd mass: 368.1611. Calcd for  $C_{16}H_{14}O_3$  (ketone): 254.0943; obsd mass: 254.0945.

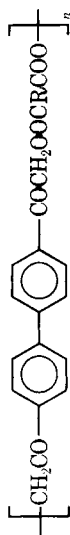
TABLE I  
 Polyesters from 4,4'-Bis(chloroacetyl)diphenyl Ether



Polymer	R	Solvent	Temperature		Yield (%)	[ $\eta$ ] <sup>a</sup>	$T_m$ (°C)
			(°C)	Time (hr)			
7		DMF - Et <sub>3</sub> N	0	48	72	insoluble	230
8	-(CH <sub>2</sub> ) <sub>4</sub> -	DMF + Et <sub>3</sub> N	0	48	78	0.12	155
9	-(CH <sub>2</sub> ) <sub>4</sub> -	NMP + Et <sub>3</sub> N	0	48	84	0.20	165
10	-(CH <sub>2</sub> ) <sub>4</sub> -	NMP + Et <sub>3</sub> N	80	18	58	0.24	180
11	-(CH <sub>2</sub> ) <sub>6</sub> -	NMP + Et <sub>3</sub> N	80	18	75	0.00	145
12	-(CH <sub>2</sub> ) <sub>7</sub> -	NMP + Et <sub>3</sub> N	0	48	90	0.21	145
13	-(CH <sub>2</sub> ) <sub>8</sub> -	DMF + Et <sub>3</sub> N	0	48	80	0.15	165
14	-(CH <sub>2</sub> ) <sub>8</sub> -	NMP + Et <sub>3</sub> N	80	18	89	0.15	150
15	-(CH <sub>2</sub> ) <sub>8</sub> -	NMP + Li <sub>2</sub> CO <sub>3</sub>	80	24	81	0.26	160
16	-(CH <sub>2</sub> ) <sub>10</sub> -	NMP + Et <sub>3</sub> N	80	18	83	0.15	150

<sup>a</sup> Intrinsic viscosities in *m*-cresol at 38.4°C.

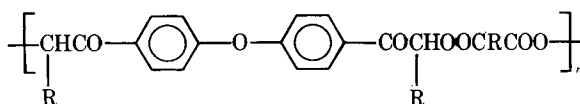
TABLE II  
 Polyesters from 4,4'-Bis(bromoacetyl)diphenyl (2)



Polymer	R	Solvent	Temperature (°C)	Time (hr)	Yield (%)	$[\eta]^a$	$T_m$ (°C)
17	-(CH <sub>2</sub> ) <sub>8</sub> -	NMP + Et <sub>3</sub> N	80	18	49	0.15	155
18	-(CH <sub>2</sub> ) <sub>10</sub> -	NMP + Et <sub>3</sub> N	80	18	23	0.07	95

<sup>a</sup> Intrinsic viscosities at 38.4°C in *m*-cresol.

TABLE III  
Polyesters from 4,4'-Bis(2-bromopropionyl)diphenyl Ether (3)



Polymer	R	Solvent	Temperature (°C)	Time (hr)	Yield (%)	$[\eta]^a$
19	-(CH <sub>2</sub> ) <sub>8</sub> -	NMP + Et <sub>3</sub> N	80°	24	49	0.12
20	-(CH <sub>2</sub> ) <sub>10</sub> -	NMP + Et <sub>3</sub> N	80°	24	14	0.13

<sup>a</sup> Intrinsic viscosities at 38.4°C in *m*-cresol.

For (6), Calcd for C<sub>24</sub>H<sub>28</sub>O<sub>5</sub> (monoester): 396.1936; obsd mass: 396.1929. Calcd for C<sub>18</sub>H<sub>18</sub>O<sub>3</sub> (ketone): 282.1255; obsd mass: 282.1248.

### Polymers

Polyesters were ground up and sifted through a 60-mesh screen. The photochemical apparatus used was the same as that used for the model compounds. The polymers were not soluble in any suitable solvent for photolysis and were not film forming from solution (TFA, *m*-cresol). The polymers (1–2 g) were photolyzed in suspension with constant stirring. The conditions of photolysis are shown in Table IV.

### Biodegradation Testing with Microorganisms

For biodegradability studies, powdered samples of model compounds and polymers (0.1 g, in duplicate) were weighed into petri dishes. Samples were incubated with *Aspergillus niger* or *Aspergillus flavus* suspended in a basal salt solution for four weeks at 30°C. The concentration of *Aspergillus niger* was 1 × 10<sup>6</sup> spore/ml and that of *Aspergillus flavus* was 1 × 10<sup>5</sup> spore/ml. The extent of fungal growth on the polymer surface was recorded according to an ASTM method.

For combined photo- and biodegradability studies, samples were dissolved in trifluoroacetic acid and in petri dishes. The acid was carefully evaporated to leave even coatings of polymer. Samples were prepared in duplicate and half were irradiated at a uniform distance (2.4 in.) from a 450-W Hanovia mercury vapor

TABLE IV  
Photolysis of Polyesters

Polymer	Filter	Dispersing medium	$[\eta]^a$
14		(stirred in H <sub>2</sub> O)	0.15 <sup>b</sup>
14		(stirred in EtOH)	0.14 <sup>c</sup>
14	Pyrex 7740	H <sub>2</sub> O/air	0.16
14	Pyrex 7740	H <sub>2</sub> O/N <sub>2</sub>	0.19
14	Pyrex 7740	EtOH/N <sub>2</sub>	0.17
15	quartz	EtOH/N <sub>2</sub>	insoluble

<sup>a</sup> Intrinsic viscosities in *m*-cresol at 38.4°C.

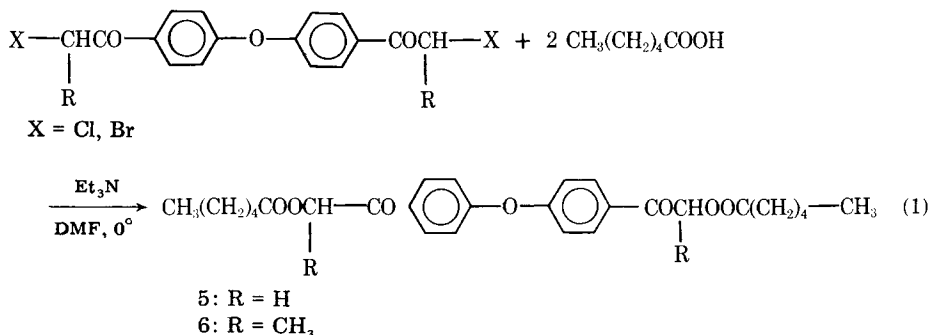
<sup>b</sup> Stirred in water 24 hr, filtered, dried, and dissolved in *m*-cresol. Same treatment as photolyzed polymers, except for irradiation.

<sup>c</sup> Same as above, except the dispersing medium was ethanol.

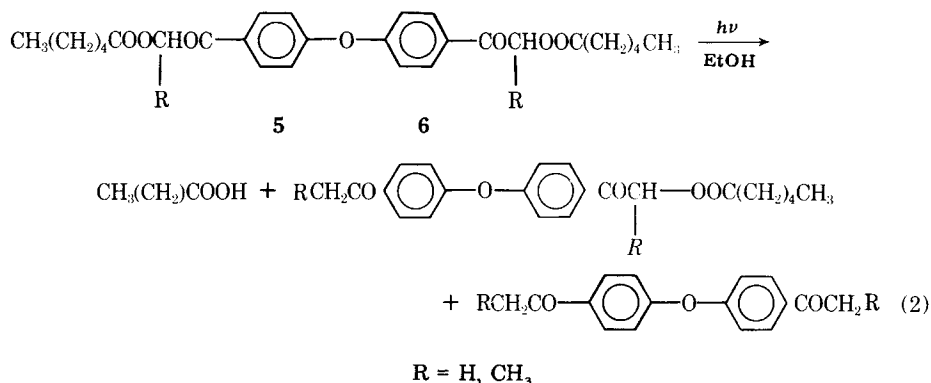
lamp water-cooled jacket through Pyrex for 24 hr. Then the samples were inoculated with spores as described above.

## RESULTS AND DISCUSSION

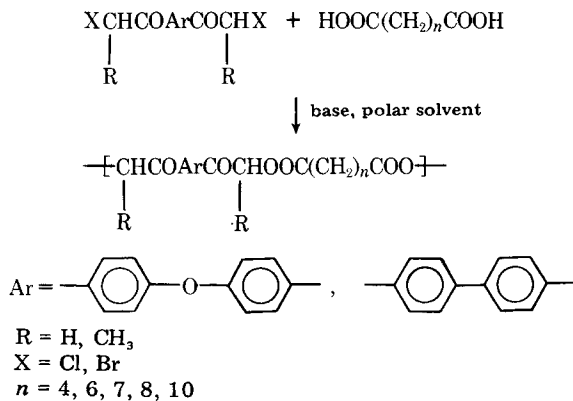
The model compounds (5) and (6) were prepared according to eq. (1):



Photolysis of (5) and (6) in ethanol gave hexanoic acid keto esters and diketones, suggesting cleavage of the ester C—O bond, eq. (2). This is consistent with results of Sheehan's method in removal of phenacyl protecting group of amino acids by photolysis.



Oligomeric poly(arylene keto esters) were prepared according to eq. (3). Their properties are shown in Tables I-III.





The polymers are soluble in trifluoroacetic acid and *m*-cresol but are insoluble in nonacidic organic solvents. Intrinsic viscosities of the polymers were found to be 0.08 to 0.26. End-group analysis indicated  $\bar{M}_n$  around 2000 for the polymers.

Photolysis of samples of polymers suspended in water or ethanol gave unexpected results. There was no detectable weight loss of the sample after photolysis. The intrinsic viscosities of the samples were found to have increased after photolysis with the exception of polymer 15 where the sample became insoluble after photolysis (Table IV). These results suggested that instead of photodegradation, coupling with some crosslinking was the major consequence of the photolysis. The close packing of the polymer chains apparently provided opportunity for the polymer radicals to couple with each other. In the case of monomeric model compounds the photolysis carried out in dilute solution radical intermediate had much less chance to react with each other, resulting in fragmentation of radicals instead of coupling. The absence of  $\gamma$ -hydrogen to the keto group eliminated the possibility of a Norrish II process. Apparently the only available Norrish I resulted in radicals that undergo coupling reaction.

The ability for the polymer sample to support the growth of the fungi *Aspergillus niger* and *Aspergillus flavus* as the only available carbon nutrient source was studied. The only growth of *Aspergillus flavus* was found on incubated sample of polymer 17. On the other hand, most of the polymers were found to be assimilated by *Aspergillus niger* (Table V). Photolysis had little effect on the biodegradation of the polymers. The change of molecular weights of polymers by photolysis were not large enough to significantly alter the biodegradability of the polymers.

In summary, a series of poly(arylene keto esters) were prepared and found to be degradable by *Aspergillus niger*. This presents a rare case of aromatic

TABLE V  
Growth of *Aspergillus niger* on Polymer Films before and after Photolysis<sup>a</sup>

Polymer	R	R'	Before	After
8	(CH <sub>2</sub> ) <sub>4</sub>	H	1	0
10	(CH <sub>2</sub> ) <sub>4</sub>	H	0	1
11	(CH <sub>2</sub> ) <sub>6</sub>	H	2	2
12	(CH <sub>2</sub> ) <sub>7</sub>	H	1	1
13	(CH <sub>2</sub> ) <sub>8</sub>	H	1	1
14	(CH <sub>2</sub> ) <sub>8</sub>	H	2	2
15	(CH <sub>2</sub> ) <sub>8</sub>	H	1	0
16	(CH <sub>2</sub> ) <sub>10</sub>	H	3	3
19	(CH <sub>2</sub> ) <sub>8</sub>	CH <sub>3</sub>	0	1
20	(CH <sub>2</sub> ) <sub>10</sub>	CH <sub>3</sub>	0	1

17	(CH <sub>2</sub> ) <sub>8</sub>	H	3	3
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<sup>a</sup> ASTM rating: 0 = no visible growth; 1 = 10% surface growth; 2 = 10–30% growth; 3 = 30–60% surface growth; 4 = 60–100% surface growth. Incubation time: 4 weeks.

polymers that have been found to be biodegradable. Photolysis of solid polymer sample resulted mostly in coupling reaction which increased the molecular weight slightly without affecting the biodegradability of the polymers. It is interesting to note that our recent study showed that benzylated polymers also undergo photocrosslinking.<sup>9</sup> Poly(keto amines) prepared from bis-haloketones undergo photodegradation but not biodegradation.<sup>12</sup>

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