

Photodegradable Polymers: Poly(arylene Keto Amine)s

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Synopsis

Low-molecular-weight poly(arylene keto amines) were prepared from the polymerization of 4,4-bis(chloroacetyl)diphenyl ether, 4,4'-bis(bromoacetyl)diphenyl ether, and 4,4'-bis(2-bromopropionyl)diphenyl ether with piperazine, 4,4'-trimethylenedipiperidine, and *N,N'*-dimethyl-1,3-propanediamine. These film-forming polymers and suitable monomeric model compounds were found to be degraded by photolysis. The poly(keto amines) resisted degradation by the fungi *Aspergillus niger* and *Aspergillus flavus*.

INTRODUCTION

Many of the reported studies on the degradation of polymers have been initiated with the goal of preventing or slowing down degradation so that their useful lifetime in the environment can be extended. However, the increasingly serious problem of disposing of nondegradable polymer wastes has motivated some of the more recent studies on photo- and biodegradable polymers.¹⁻⁴ Since low-molecular-weight materials can be assimilated more easily than their high-molecular-weight analogs by soil microorganisms, one of the approaches to biodegradable polymers has been the incorporation of photosensitive groups into the polymer chains to make the polymers photodegradable. The Ecolytes series of keto group-containing olefin polymers are good examples of this approach.¹

In addition, there has been a need for photodegradable polymers in recent years in the electronics industry, and the availability of such polymers has undoubtedly contributed to advances in that field.⁵⁻⁹

We have recently reported on the effects of some structural variations on the combined photodegradation and biodegradation of step growth polymers.¹⁰ We report here the synthesis and photodegradation of poly(arylene keto amines) designed to be photodegradable.

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 spec-

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trophotometer. Elemental analyses were performed by Baron Consulting Co. of Orange, CT.

Reagents

The following chemicals were obtained from Aldrich Chemical Co., Milwaukee, WI: bromoacetyl bromide, α -bromo-*p*-methoxyacetophenone, 2-bromopropionyl chloride, chloroacetyl chloride, *m*-cresol, diphenyl ether, hexamethylphosphoramide, *N*-methylpyrrolidone, piperazine, and 4,4'-trimethylenedipiperidine. *N,N'*-Dimethyl-1,3-propanediamine was obtained from Air Products and Chemicals, Allentown, PA.

Solvents were purified by recommended procedures prior to use.¹¹ Sabouraud's and dextrose agars were obtained from Difco, Detroit, MI. *Aspergillus niger* strain 9642 and *Aspergillus flavus* strain 9643 were obtained from American Type Culture Collection, Rockville, MD.

Synthesis

The syntheses of 4,4'-bis(chloroacetyl)diphenyl ether (1),¹² 4,4'-bis(2-bromoacetyl)diphenyl ether (2),^{13,14} and 4,4'-bis(2-bromopropionyl)diphenyl ether (3) are described in a preceding article.¹⁵

α -Bromo-*p*-methoxypropiophenone (4). The method mentioned above was used to synthesize this compound, using 13.35 g (0.01 mol) anhydrous aluminum chloride, 21.6 g (0.01 mol) 2-bromopropionyl bromide in 15 mL methylene chloride, and 10.8 g (0.01 mol) anisole in 15 mL methylene chloride. The yield was 8.09 g (33.29%), mp 64.5–66.5°C (lit. 66–667°C).¹⁶

ANAL. Calcd. for C₁₀H₁₁BrO₂: C, 49.38; H, 4.53; Br, 32.92. Found: C, 49.66; H, 4.79; Br, 32.41.

Model amine 5. In a 100-mL round-bottomed flask were mixed 8 g α -bromo-*p*-methoxyacetophenone (0.035 mol) and 3.01 g (0.035 mol) piperazine in 35 mL *N*-methylpyrrolidone. The flask was warmed on the steam bath for 6 h and the contents were poured into 300 mL 0.5 *M* ammonium hydroxide with stirring. The solid was filtered, washed with distilled water, and dried under vacuum 48 h at 50°C. The yield was 1.48 g (22.12%), mp 145–154°C.

ANAL. Calcd. for C₂₂H₂₆N₂O₄: C, 69.11; H, 6.81; N, 7.33. Found: C, 69.31; H, 6.75; N, 7.38.

Model amine 6. This material was prepared in two ways. In the first method, an attempt was made to prepare α -chloro-*p*-methoxypropiophenone. The procedure was similar to that used for 4,4'-bis(chloroacetyl)diphenyl ether (1) using 12.1 g (0.09 mol) anhydrous aluminum chloride, 11.5 g (0.09 mol) 2-chloropropionyl chloride, and 9.78 g (0.09 mol) anisole in 20 mL methylene chloride. This compound is a low-melting material which could not be recrystallized, and it is also a severe skin irritant. It was thus used as is in the following procedure. This material (assuming 50% yield) as well as 3.5 g (0.04 mol) piperazine was dissolved in 40 mL *N*-methylpyrrolidone and warmed on the steam bath 12 h. The resulting slurry was poured into 300 mL 0.5 *M* ammonium hydroxide with stirring. An oil formed which, on drying under vacuum 48 h at 50°C, became solid. It was recrystallized three times from 2-propanol to yield 0.61 g (7.44%) cream-colored crystals, mp 138–145°C.

ANAL. Calcd. for C₂₄H₃₀N₂O₄: C, 70.24; H, 7.32; N, 6.83. Found: C, 69.96; H, 7.47; N, 6.63.

In the second method, the procedure above in *N*-methylpyrrolidone was repeated using 4.86 g (0.02 mol) α -bromo-*p*-methoxypropiophenone (4), 1.72 g (0.02 mol) piperazine, and 25 mL *N*-methylpyrrolidone. The yield was 0.88 g (21.46%), mp 132–138°C.

ANAL. Calcd. for $C_{24}H_{30}N_2O_4$: C, 70.24; H, 7.32; N, 6.83. Found: C, 70.06; H, 7.45; N, 6.74.

It should be noted that these two methods of synthesis produce mixtures of diastereomers, since there are two asymmetric centers in model amine 6. This accounts for the ranges and differences in melting temperatures.

Polymers. The syntheses of the polymers are summarized in Table I. The method was similar to that of DiChamp, Tortai, and Marechal,¹⁷ who prepared some polymers from the diphenyl ether derivatives using primary diamines.

General procedure. Reactants listed in Table I (0.3 mol each of ketone and amine and a stoichiometric quantity of base) were dissolved in 150–200 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 to 80–90°C in an oil bath, and this temperature was maintained for the indicated time. The flask was cooled under nitrogen overnight and the solid precipitate was filtered off. The filtrate was poured into 3–4 mL acetone with stirring. The yellow polymer was collected with suction and washed with a large quantity of acetone, 0.5 *M* ammonium hydroxide, and distilled water. Ammonium hydroxide was used to neutralize amine hydrochloride in the polymer. In most cases, some hydrochloride remained even after repeated washings. The polymer was dried in vacuo 48 h at 50°C. Yields and melting temperatures are shown in Table I.

Photolysis Studies of Model Compounds

Model compounds 5 and 6 (0.03 g) were each dissolved in 290 mL 1% aqueous methanol. Photolysis through Pyrex in a photochemical reaction apparatus from Ace Glass Co., Inc., proceeded 12 h. A 450-W Hanovia lamp was used as the light source. The reaction slowed down considerably after 12 h. The solvent was evaporated and the residue was dissolved in methylene chloride. Column chromatography on silica gel yielded the ketone photolysis product and a mixture of other products.

For model 5, the reaction yielded 20% *p*-methoxyacetophenone, which was identified by high-resolution mass spectrometry. Calcd. for $C_9H_{10}O_2$: 150.0681. Observed mass: 150.0680.

For model 6, the reaction yielded 45% *p*-methoxypropiophenone, which was identified in the same way. Calcd. for $C_{10}H_{12}O_2$: 164.0837. Observed mass: 164.0849.

The yields of these products were estimated by integration of the NMR spectra of the reaction mixtures after photolysis.

Polymer Photolysis

Each polymer (0.5 g) was dissolved in 2–3 mL formic acid on a Teflon sheet. The formic acid was evaporated slowly at room temperature and then under vacuum for three days until constant weight was obtained.

Films were photolyzed 24 h at a uniform distance (2.4 in.) from the Hanovia

TABLE I
 Synthesis of Polymers

Polymer No.	Solvent/base	Time, h	Yield, %	$[\eta]$, dL/g ^a	T_m , °C
(a) Polyamines from 4,4'-Bis(chloroacetyl)diphenyl Ether (1)					
Compound 1 and Piperazine					
7	HMPA-amine	1	32	0.21	160
8	NMP-amine	1	65	0.21	165
9	NMP-Li ₂ CO ₃	1	11	0.24	175
10	NMP-Li ₂ CO ₃	1	35	0.29	180
11	DMA-Li ₂ CO ₃	1	3	—	200
12	NMP-Li ₂ CO ₃	3	56	0.15	160
13	NMP-Li ₂ CO ₃	3	61	0.14	150
14	NMP-Et ₃ N	24	83	0.22	160
15	NMP-Li ₂ CO ₃	24	45	0.17	150
Compound 1 and <i>N,N'</i> -Dimethyl-1,3-propanediamine					
16	HMPA-amine	1	19	0.10	140
17	NMP-Li ₂ CO ₃	3	44	— ^b	180
Compound 1 and Trimethylenedipiperidine					
18	NMP-amine	1	76	0.21	130
19	NMP-Li ₂ CO ₃	3	73	0.15	150
(b) Polyamines from 4,4'-Bis(bromoacetyl)diphenyl Ether (2) and Piperazine					
20	NMP-Li ₂ CO ₃	24	61	0.20	155
Compound 2 and Trimethylenedipiperidine					
21	NMP-Li ₂ CO ₃	24	77	0.21	200
(c) Polyamines from 4,4'-Bis(2-bromopropionyl)diphenyl Ether (3) and Piperazine					
22	NMP-Li ₂ CO ₃	24	31	0.09	140
Compound 3 and Trimethylenedipiperidine					
23	NMP-Li ₂ CO ₃	24	70	0.15	170

^a Intrinsic viscosities at 38.4° in *m*-cresol.

^b Insoluble.

TABLE II
 Photolysis of Polyamines

Polymer	Filter	Time, h	$[\eta]$ un, dL/g ^{a,b}	$[\eta]$ p, dL/g ^{a,c}
			$\left[\text{N} \begin{array}{c} \diagup \quad \diagdown \\ \diagdown \quad \diagup \end{array} \text{N} - \text{CH}_2 \text{C} \begin{array}{c} \text{O} \\ \parallel \end{array} \text{Ph} \text{O} \text{Ph} \text{C} \begin{array}{c} \text{O} \\ \parallel \end{array} \text{CH}_2 \right]_n$	
12	Pyrex 7740	24	0.15	0.15
14	quartz	24	0.17	0.13
			$\left[\text{N} \begin{array}{c} \diagup \quad \diagdown \\ \diagdown \quad \diagup \end{array} \text{N} - \text{CH}_2 \text{CH}_2 \text{CH}_2 - \text{N} \begin{array}{c} \diagup \quad \diagdown \\ \diagdown \quad \diagup \end{array} \text{N} - \text{CH}_2 \text{C} \begin{array}{c} \text{O} \\ \parallel \end{array} \text{Ph} \text{O} \text{Ph} \text{C} \begin{array}{c} \text{O} \\ \parallel \end{array} \text{CH}_2 \right]_n$	
18	Pyrex 7740	21	0.21	0.20
19	quartz	24	0.20	0.15
			$\left[\text{N} \begin{array}{c} \diagup \quad \diagdown \\ \diagdown \quad \diagup \end{array} \text{N} - \text{CH}(\text{CH}_3) \text{C} \begin{array}{c} \text{O} \\ \parallel \end{array} \text{Ph} \text{O} \text{Ph} \text{C} \begin{array}{c} \text{O} \\ \parallel \end{array} \text{CH}(\text{CH}_3) \right]_n$	
22	Pyrex 7740	24	0.09	0.06
			$\left[\text{N} \begin{array}{c} \diagup \quad \diagdown \\ \diagdown \quad \diagup \end{array} \text{N} - \text{CH}_2 \text{CH}_2 \text{CH}_2 - \text{N} \begin{array}{c} \diagup \quad \diagdown \\ \diagdown \quad \diagup \end{array} \text{N} - \text{CH}(\text{CH}_3) \text{C} \begin{array}{c} \text{O} \\ \parallel \end{array} \text{Ph} \text{O} \text{Ph} \text{C} \begin{array}{c} \text{O} \\ \parallel \end{array} \text{CH}(\text{CH}_3) \right]_n$	
23	Pyrex 7740	24	0.15	0.12

^a Intrinsic viscosities at 38.4°C in *m*-cresol.

^b Unphotolyzed.

^c Photolyzed.

lamp water-cooled jacket. The polymers were ground up and their intrinsic viscosities were measured in *m*-cresol at 38.4°C. The viscosities of the photolyzed polymers were compared to those of polymers which had undergone the same procedure except for photolysis. The conditions of photolysis are shown in Table II.

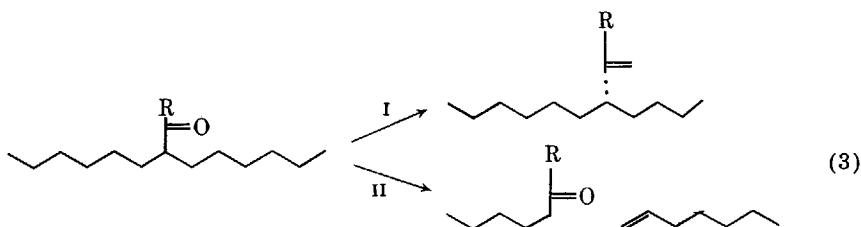
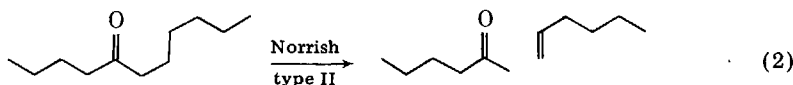
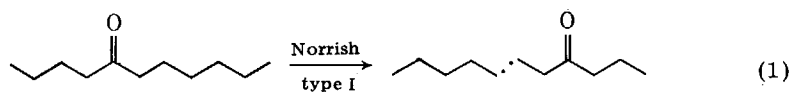
Combined Photo- and Biodegradation Studies

Films (0.1 g) were prepared from formic acid in Petri dishes, and half of them were irradiated through Pyrex at a uniform distance of 2.4 in. from the Hanovia lamp jacket for 24 h. Both irradiated and unirradiated samples (in duplicate) were inoculated with *Aspergillus niger* or *Aspergillus flavus* according to established procedures.^{10,18}

RESULTS AND DISCUSSION

The most frequently used photosensitive group in photodegradable polymers is the aliphatic ketone.¹⁹⁻²² The primary photoreactions of the keto group include the Norrish type I or Norrish type II processes, depicted in eqs. (1), (2),

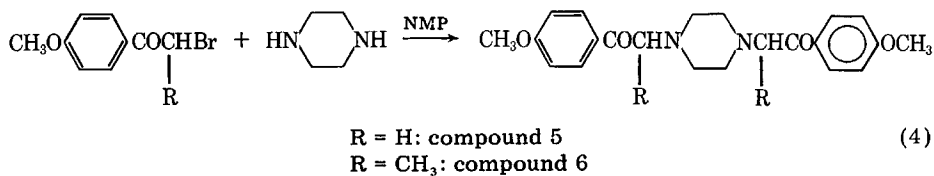
and (3):



The Norrish type I reaction can result in crosslinking, but the type II reaction always results in polymer chain cleavage. For a Norrish type II reaction to occur, a hydrogen located at the α -position to the keto group is necessary.

Since Hyatt²³ has reported the Norrish type II reaction of phenacylamines, we decided to prepare model compounds and polymers containing phenacylamine groups and to test their photodegradability.

Haloketones 1–4 were prepared by reactions of haloacid chlorides with aromatic hydrocarbons. Compounds 1–3 were used in the polymerization described in this report. Compound 4 was used in the preparation of model compound 6. Model compounds 5 and 6 were prepared according to eq. (4):



The photolysis of compound 5 gave 20% *p*-methoxyacetophenone. Under the same conditions, 45% *p*-methoxypropiophenone was generated from the photolysis of compound 6. This result may be in conflict with reports that α -substituents retard the type II cleavage reaction.²²

The poly(keto amines) were prepared from the polymerization of bishaloketones 1–3 with secondary diamines piperazine, 4,4'-trimethylenedipiperidine, and *N,N'*-dimethyl-1,3-propanediamine carried out in polar, nonprotic solvents at 80–90°C.

Results of the polymer syntheses are listed in Table I. Secondary diamines were chosen over primary diamines to avoid crosslinking. The resulting polymers were found to be soluble in *m*-cresol, with the exception of polymer 17. The intrinsic viscosities (in *m*-cresol) indicated that most of the polymers have low molecular weights. Endgroup titration suggested \bar{M}_n around 2000. Polymer 17 was found to be insoluble but swelled in *m*-cresol. It is quite possible that it was crosslinked by enamine formation.

The polymers were photolyzed by irradiation with the light generated from a Hanovia 450-W medium-pressure mercury lamp. The results of the photolysis are listed in Table II. Most of the polymer samples were degraded as indicated by the decreased intrinsic viscosities after photolysis. Photodegradation was more efficient when a quartz filter was used than when a Pyrex filter was used for the photolysis. Since the UV spectra of model compounds 5 and 6 in ethanol exhibited λ_{\max} around 275 nm and a tailing off of absorption into the region above 300 nm, it was not unexpected that more degradation took place under irradiation through quartz. Only radiation with wavelength greater than about 300 nm passes through a Pyrex filter.

Polymers 22 and 23 were degraded when irradiated through a Pyrex filter, whereas the other polymers were not. This may be attributed to several factors, including the presence of the α -methyl substituents, which contributed to greater photoreactivity for model 6 than for model 5. In addition, polymers 22 and 23 are of lower molecular weight than the other polymers photolyzed and are completely amorphous, due to the presence of asymmetric centers in the molecules. X-Ray powder patterns for polymers 13 and 19 showed that they were about 10% crystalline or less.

Polymers of the type described in this report might be useful for preparing positive photoresists because, while the higher-molecular-weight poly(keto amines) would not be soluble in dilute aqueous acids, the lower-molecular-weight photolysis products might be.

It is interesting to compare the results of photolysis of the poly(arylene keto amines) with those for structurally similar poly(arylene keto esters).¹⁵ The absence of hydrogen bonded to the α -carbon in the poly(keto esters) eliminated the possibility of a Norrish type II reaction. As a result, coupling and crosslinking were the major reactions of the photolysis. Another difference between the two series of polymers is the fact that the hydrolyzable poly(arylene keto esters) were degraded by the fungi *Aspergillus niger* and *Aspergillus flavus*, whereas the nonhydrolyzable poly(arylene keto amines) were found to resist degradation by the same fungi, both before and after photolysis.

The authors thank the National Science Foundation (Grant DMR78-13402) for support of this research. This article was abstracted from the Ph.D. dissertation of C. A. Byrne, University of Connecticut, 1978.

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Received September 28, 1981

Accepted December 28, 1981