

NOTES

Simple Synthesis of Polyketones Containing Anthraquinone Units

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Much work has been published on the synthesis of condensation polymers containing quinone or anthraquinone units. Cassidy *et al.* have prepared polyurethanes and polycarbonates from quinonediols and their redox behavior has been studied.¹ Marvel and his coworkers have synthesized a series of thermally stable ladder or partially ladder polymers from tetraaminoanthraquinones and showed that the introduction of anthraquinone units into polymers permits the solubilization of the polymers by reduction of the quinone groups.²

However, most of the published methods for the incorporation of a quinone or anthraquinone into polymer backbones involve tedious synthetic steps such as the introduction of various functional groups into the quinone or anthraquinone moieties.

In our earlier publications, it was demonstrated that phosphorus pentoxide/methanesulfonic acid (PPMA) in a weight ratio of 1 : 10 as a substitute for poly(phosphoric acid) (PPA) is a very useful dehydrating agent for the preparation of various types of condensation polymers, such as polyether-sulfone,³ polyketones,⁴ and poly(benzazole)s.⁵ Furthermore, this method was successfully applied to the simple synthesis of polyketones containing crown ether units.⁶ In order to extend the

preparative utility of this method, we applied it to the synthesis of polyketones containing anthraquinone units.

This article describes a successful synthesis of polyketones containing anthraquinone units by the direct polycondensation of dicarboxylic acids with 1,5-diphenoxyanthraquinone using PPMA which acts as condensing agent and solvent.

EXPERIMENTAL

Materials

The reagent PPMA was prepared according to the reported procedure.⁷ Various substituted benzoic acids **1a**—**1e** of reagent grade were used as received. Dicarboxylic acids **4a**—**4c** were purified by recrystallization. 4,4'-Oxybisbenzoic acid (**4e**) was prepared by the reaction of diphenyl ether with oxalyl chloride.⁸ Crystallization from acetic acid yielded white crystals. mp 337°C (by DTA) (lit.⁸ 331—333°C). 4-Methoxyisophthalic acid (**4d**) was prepared through oxidation of the corresponding 2,4-dimethyl anisole with potassium permanganate in pyridine-water. Crystallization from water gave white crystals. mp 284°C (by DTA) (lit.⁹ 261°C). 1,5-diphenoxyanthraquinone (**2**) (supplied by Mitsubishi Chemical Industries Ltd.) was crystallized from nitro-

benzene. Brown needles; mp 222°C (by DTA) (lit.¹⁰ 215°C).

Model Reaction

1,5-Bis(p-benzoylphenoxy)anthraquinone (3a). A mixture of **2** (0.392 g, 1.0 mmol) and benzoic acid **1a** (0.244 g, 2.0 mmol) in PPMA (3 ml) was stirred at 70°C for 3 h. The solution was poured into ice-water (300 ml) and neutralized with sodium carbonate. The product was filtered, washed with water, and dried. The yield was 0.599 g (99%). Recrystallization from toluene produced yellow crystals, mp 263°C (by DTA). The IR spectrum (KBr) showed absorptions at ν 1650 (C=O), and 1240 cm^{-1} (C–O–C). *Anal.* Calcd for $\text{C}_{40}\text{H}_{24}\text{O}_6$: C, 79.99%; H, 4.36%. Found: C, 80.12%; H, 4.18%.

1,5-Bis[p-(m-methylbenzoyl)phenoxy]anthraquinone (3b). This compound was prepared from **2** and *m*-methylbenzoic acid (**1b**) in a mole ratio of 1:2 as described above. The yield was 99%. Recrystallization from toluene produced yellow crystals, mp 231°C (by DTA). The IR spectrum exhibited absorptions at ν 1650 (C=O) and 1230 cm^{-1} (C–O–C). *Anal.* Calcd for $\text{C}_{42}\text{H}_{28}\text{O}_6$: C, 80.24%; H, 4.49%. Found: C, 80.76%; H, 4.64%.

1,5-Bis[p-(p-methoxybenzoyl)phenoxy]anthraquinone (3c). This compound was synthesized from **2** and *p*-methoxybenzoic acid **1c** in a yield of 99%. Recrystallization from toluene gave yellow crystals, mp 248°C (by DTA). *Anal.* Calcd for $\text{C}_{42}\text{H}_{28}\text{O}_8$: C, 76.36%; H, 4.27%. Found: C, 76.4%; H, 4.3%.

Polymer Synthesis

Typical examples of polymerizations follows.

Polymer (5a) from 2 and 4a. A solution of **2** (0.392, 1.0 mmol) and **4a** (0.202 g, 1.0 mmol) in PPMA (3 ml) was stirred at 60°C for 30 min. The resulting viscous solution was diluted with methanesulfonic acid. The solution was poured into water and neutralized with sodium carbonate. The fibrous polymer was col-

lected, washed with hot water, and refluxed in water 2 h. The polymer was dried in vacuum at 100°C for 2 d. The yield was essentially quantitative. The inherent viscosity of the polymer, in concentrated sulfuric acid was 0.70 dl g^{-1} , as measured at a concentration of 0.5 g dl^{-1} at 30°C. The IR spectrum (KBr) exhibited absorptions at ν 1680 (C=O), and 1240 cm^{-1} (C–O–C). *Anal.* Calcd for $(\text{C}_{36}\text{H}_{30}\text{O}_6)_n$: C, 74.98%; H, 5.59%. Found: C, 74.8%; H, 5.6%.

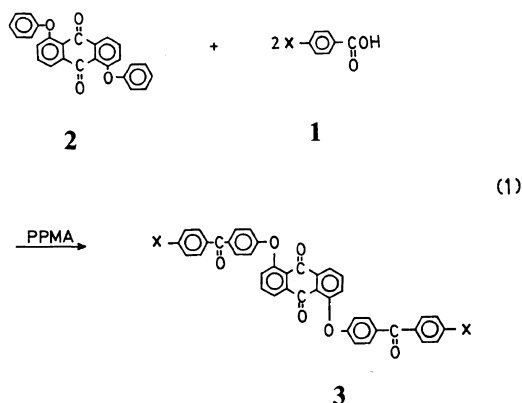
Polymer (5e) from 2 and 4e: Polymer **5e** was prepared from **2** and **4e** at 70°C for 24 h as described above. The polymer, obtained in nearly quantitative yield, had an inherent viscosity of 0.79 dl g^{-1} in concentrated sulfuric acid (0.5 g dl^{-1} at 30°C). The IR spectrum (KBr) showed absorptions at ν 1650 (C=O), and 1240 cm^{-1} (C–O–C). *Anal.* Calcd for $\text{C}_{48}\text{H}_{22}\text{O}_7 \cdot 1/2\text{H}_2\text{O}$: C, 77.04%; H, 3.72%. Found: C, 76.60%; H, 3.73%.

RESULTS AND DISCUSSION

Model Reaction

In order to obtain information regarding the reaction conditions necessary for polymer formation and to obtain model compounds to aid in polymer identification, we first studied the reaction of 1,5-diphenoxyanthraquinone **2** with benzoic acid **1a** in a 1:2 mole ratio over temperature range at 20–100°C. The reaction was performed by dissolving **2** and **1a** in PPMA. After the reaction was completed, the solution was poured into water and neutralized with sodium carbonate, and the crude product was filtered. These preliminary experiments showed that the condensation was completed in 3 h at 70°C and 3 ml of PPMA were found to be enough for the reaction on a 1.0 mmol of **2**.

On the basis of these results, the reaction of substituted benzoic acid **1** with **2** was carried out at 70°C in PPMA (eq 1).



X: H, **1a**; CH₃, **1b**; CH₃O, **1c**; Cl, **1d**; NO₂, **1e**.

The data summarized in Table I indicate that **2** is easily acylated by benzoic acids containing electron-donating groups and produced quantitative yields of the expected ketones. Benzoic acids with electron-withdrawing groups reacted slowly with **2** and gave a mixture of mono- and dibenzoyl compounds. These findings of substituent effects of benzoic acids are explained by the stability of the reaction intermediates, acylium ions, as described in the previous papers.^{4,5}

Polymer Synthesis

To determine the optimum conditions for the polymerizations, the effect of the reaction temperature on the inherent viscosity of the resulting polymer was studied over the temperature range 60–100°C by the polymerization of **2** with 4,4'-oxybisbenzoic acid **4e**. As shown in Table II, the polycondensation at 70°C gave the polymer with an inherent viscosity as high as 0.79 dl g⁻¹ in 24 h. The polycondensation proceeded with the formation of a clear brown solution at a temperature lower than 70°C, but at around 100°C the solution became dark brown, probably because of decomposition of the monomer.

Table III lists the effects of the amount of PPMA on the polycondensation. Three milliliters of PPMA were found to be adequate for

Table I. Preparation of ketones **3** in PPMA^a

Substituted benzoic acid	Product	
	Type	Yield/%
1a	3a	99
1b	3b	99
1c	3c	99
1d		— ^b
1e		— ^b

^a Reaction was carried out with 1.0 mmol of **2** and 2 mmol of **1a** in PPMA (3 ml) at 70°C for 3 h.

^b A mixture of mono- and diacylated compounds was obtained.

Table II. Effects of reaction temperature on polycondensation^a

Reaction conditions			Polymer
Temp/°C	Time/h	PPMA/ml	$\eta_{inh}/dl\ g^{-1\ b}$
60	48	5	0.44
60	24	3	0.51
70	48	5	0.47
70	24	3	0.79
80	48	5	0.31
100	48	5	0.11

^a Polycondensation was carried out with 1.0 mmol of each monomer.

^b Measured at a concentration of 0.5 g dl⁻¹ in concentrated sulfuric acid at 30°C.

Table III. Effects of the amount of PPMA on polycondensation^a

Reaction conditions		Polymer
PPMA/ml	Time/h	$\eta_{inh}/dl\ g^{-1\ b}$
2	12	0.30
3	12	0.64
3	24	0.79
5	24	0.33
7	24	0.24

^a Polycondensation was carried out with 1.0 mmol of each monomer at 70°C.

^b Measured at a concentration of 0.5 g dl⁻¹ in concentrated sulfuric acid at 30°C.

the reaction on a 1 mmol scale.

On the basis of these results, the direct polycondensation of **2** with dicarboxylic acids

Table V. Thermal stability of poly(ketone)s **5**

Polymer Type	Decomposition temp/°C ^a	
	In air	In N ₂
5a	390	370
5c	370	380
5e	410	410

^a 10% weight loss temperature observed by TG.

hand, polymers **5d** and **5e** were soluble in these strong acids and in polar aprotic solvents, such as *N*-methyl-2-pyrrolidone and *N,N*-dimethylacetamide.

The thermal stability of the polymers was examined by thermogravimetry (TG). A typical trace for polymer **5e** is shown in Figure 1. The polymer showed a 10% weight loss at 410°C in air. These data are summarized in Table V. These values showed aromatic polyketones containing anthraquinone units to be less thermally stable than conventional aromatic polyketones.

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