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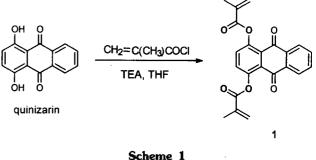# Insoluble Polymer Catalysts for Photooxidation of Amine

Jong-Man Kim, Dong-Keun Han, Chan-Woo Lee, Seong-Hyun Kim[†], Myoung-Seon Gong[†], and Kwang-Duk Ahn[*]

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Recently, organic reactions on polymer supports have gained great attention as tools for generating diverse compounds.[1-5] A key strength of the solid phase organic synthesis is the relatively easy work-up and purification steps: simple filtration allows separation of reagents, starting materials, and solvents from the desired products. We have been interested in designing efficient and inexpensive polymer catalysts which participate in photoinduced electron transfer process. We have, especially, focused on developing cross-linked polymer systems which are insoluble in common organic solvents so that we can easily remove the polymer catalysts by filtering. As preliminary results, we now report the preparation of cross-linked polymers having anthraquinone group and their application to photoinduced oxidation of benzylamine.

The anthraquinone-containing dimethacrylated quinizarin monomer QDMA 1 used in this study was prepared in a high yield from commercially available quinizarin by treatment with methacryloyl chloride (Scheme 1). The presence of methacryloyl moieties in the monomer 1 was evidenced by the appearance of ^1H NMR resonances for the vinyl protons at 5.89 and 6.42 ppm. The pale-yellow solid, QDMA 1 (70%, mp 110-112 °C) was stable over months at room temperature: IR (KBr) $v(cm^{-1})$ 2978 (aliphatic C-H), 1745, 1676 (C=O), 1322, 1132 (C-O); ^1H NMR (200 MHz, $CDCl_3$) δ 2.18 (s, 6H, $2CH_3$), 5.89 (s, 1H, $C=CH_2$), 6.42 (s, 1H, $C=CH_2$), 7.48 (s, 2H, Ar-H), 7.25 (q, 2H, Ar-H), 8.16 (q, 2H, Ar-H).

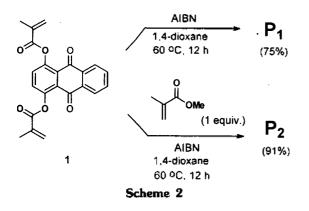Polymerization of the monomer 1 in the presence of N,N'-

Scheme 1

azobisisobutyronitrile (AIBN) in 1,4-dioxane for 12h at 60 °C provided the cross-linked polymer P_1 in 75% yield. The monomer 1 was also copolymerized with an equivalent molar ratio of methyl methacrylate (MMA) to give polymer P_2 in 91% yield (Scheme 2). The cross-linked polymer P_1 and P_2 were insoluble in organic solvents. IR (KBr) v (cm^{-1}): polymer P_1, 2929 (aliphatic C-H), 1743, 1677 (C=O), 1321, 1116 (C-O); polymer P_2, 2953 (aliphatic C-H), 1738, 1679 (C=O), 1321, 1113 (C-O).

The polymers were ground in a crucible and sieved through 150-μm sieve. The powders which passed the sieve were collected and further ground using a ball-mill machine. The resulting solid polymers were subjected to extensive extraction with hot MeCN in a soxhlet apparatus to remove unreacted monomers, oligomers and soluble impurities. The average size of the particle obtained was *ca.* 10 μm.

In order to investigate photochemical reactions of the po-

Scheme 2

lymers with benzylamine (**2**), a suspension of the polymer and benzylamine in MeCN or MeOH was exposed by UV light tuned at 260 nm. The reaction mixture was filtered to remove the polymer after irradiation and the filtrate was concentrated *in vacuo*. The residue was subjected to ^{1}H NMR analysis to monitor the reaction. As can be seen in Scheme 3 and Table 1, irradiation of the suspension of P_1 and benzylamine in MeCN for 30 min led to production of *N*-benzylidenebenzylimine (**3**) as the sole product. When methanol was employed as a solvent, much lower yield of the imine **3** was observed. The turnover numbers shown in Table 1 represent the molar ratios between the observed imine **3** and the polymer P_1 used. Similar results were obtained when P_2 was employed. The observed product **3** is presumed by condensation of benzaldehyde and benzylamime. In the reaction, benzaldehyde, which is not isolated, is produced by hydrolysis of the photooxidation product in the first step.

The multiple turnover nature of the reaction is demonstrated by the observation that more than 100% of the imine **3** based on P_1 is produced (Table 1). Control experiments have shown that benzylamine is not converted to the imine **3** when the polymer is excluded. Thus, the observed yield (*ca.* 50%) of the imine **3** from the photoreaction of P_1 (3.3×10^{-4} M) and benzylamine (1.2×10^{-2} M) indicates a nearly quantitative reaction. Clean formation of the imine **3** from the photoreaction was further de-
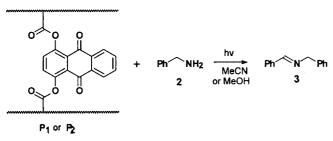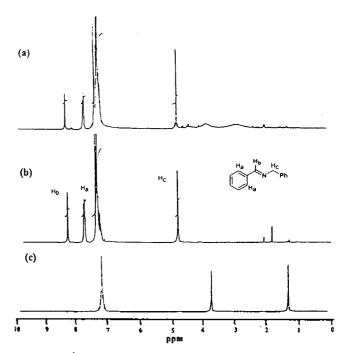
monstrated by ^{1}H NMR analysis (Figure 1). A ^{1}H NMR spectrum of crude photolysate obtained from irradiation (30 min) of P_1 (100 mg) and benzylamine (100 mg) in MeCN is shown in Figure 1(a). Peaks at 4.70, 7.60, and 8.20 ppm are diagnostic for the imine **3**. In order to prove further the structure of the obtained product, the imine **3** was independently prepared by equimolar condensation of benzaldehyde with benzylamine (Figure 1(b)): ^{1}H NMR (200 MHz, CDCl$_3$) δ 4.70 (s, 2H, PhCH$_2$), 7.15-7.40 (m, 8H, Ar-H), 7.60-7.75 (m, 2H, Ar-H), 8.20 (s, 1H, N=CH). The photoreaction product **3** was purified by column chromatography using an eluent, hexane/ethyl acetate (10/1 by vol) to give the identical ^{1}H NMR spectrum with the condensation product amine. It is not known, at this point, whether some modifications on anthraquinone groups occurred during the photoreaction. However, it was confirmed that anthraquinone moieties are at least not cleaved from the polymers since analysis of the photolysate by ^{1}H NMR reveals no aromatic resonance which correspond to anthraquinone group.

Formation of the imine **3** can be rationalized by electron transfer mechanism (Scheme 4). Thus, single electron transfer (SET) from the nitrogen of benzylamine to the excited state of anthraquinone (AQ) groups of **P1** gives the anthraquinone anion radical **4** and amine cation radical **5**. The facility of the SET step here results from the strong thermodynamic/kinetic driving force for SET from benzylamine to the excited state anthraquinone moiety.[6,7] The ion radical pairs then readily undergo proton transfer to form an anthraquinone ketyl radical **6** (AQH·) and an α-amino radical **7**. The α-amino radical **7** can be oxidized further by a second electron transfer to AQH· followed by proton

P$_1$ or P$_2$

Scheme 3

Table 1. Summary of Photoreaction of P_1 and Benzylamine **2***

P_1 (M)	2 (M)	Solvent	Turnover	3 (% yield)
3.3×10^{-5}	1.2×10^{-2}	MeCN	87	24
1.7×10^{-4}	1.2×10^{-2}	MeCN	26	37
3.3×10^{-4}	1.2×10^{-2}	MeCN	18	~50
3.3×10^{-4}	1.2×10^{-2}	MeOH	0.4	~1

*Irradiation at room temperature for 30 min.

Figure 1. ^{1}H NMR spectra (200 MHz, CDCl$_3$) of (a) the product obtained by UV irradiation of P_1 and benzylamine in MeCN followed by filtration and concentration, (b) *N*-benzylidenebenzylimine (**3**) prepared by mixing of an equimolar amount of benzaldehyde and benzylamine, and (c) benzylamine.

Scheme 4

transfer to generate the reduced dihydroxyanthracene **8** (AQH₂) and benzylimine **9**. The reduced anthraquinone AQH₂ can be oxidized to the starting AQ by molecular oxygen. The benzylimine **9** then is hydrolyzed by water in the

media to benzaldehyde **10** followed by condensation with benzylamine yielding the observed final product, *N*-benzylidenebenzylimine **3**.

In this study, anthraquinone-containing, cross-linked polymers have been applied to oxidation of benzylamine. Benzylamine was readily oxidized to benzaldehyde by the polymers upon irradiation with UV light. Since cross-linked polymer photocatalysts have unique advantages over small molecule catalysts, the results of this study might be useful in the development of new polymer photocatalysts. Application of the polymers to oxidation of secondary and tertiary amines is under progress.

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Diastereoselective Synthesis of Aryloxazinones

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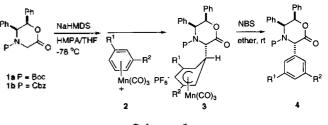*Received February 27, 1998*

An interesting and important nonproteinogenic class of amino acids are the arylglycines.[1] One of the best-studied and most interesting sources of arylglycines are the glycopeptide antibiotics. However, the arylglycines are difficult to synthesize in optically pure form due to the ease at which the α-methine proton can undergo base-catalyzed racemization.[2]

Numerous approaches to the asymmetric synthesis of arylglycines have appeared, including: asymmetric Strecker synthesis;[3] arylation or alkylation of nucleophilic glycinates;[4] arylation of electrophilic glycinates;[5] electrophilic amination of chiral enolates;[6] and nucleophilic amination of α-substituted acids,[7] amongst others.[8]

We report herein our preliminary studies on the conversion of (arene)Mn(CO)₃⁺ complexes to aryloxazinones, which can be converted to arylglycines, *via* their reaction with the Williams chiral glycine enolate equivalent (**1a** or **1b**).[9]

(Arene)Mn(CO)₃⁺ complexes (**2**) were treated with eno-

late of **1a** or **1b** to give the substituted cyclohexadienyl-Mn (CO)₃ complexes (**3**) with high diastereoselectivity. We tried to separate the cyclohexadienyl-Mn(CO)₃ complexes, but significant decomposition of cyclohexadienyl-Mn(CO)₃ complexes occurs upon attempted silica gel chromatography. So direct treatment of these reaction mixture with *N*-bromosuccinimide effected oxidative demetallation[4a,4b,10] to give the aryloxazinones (**4**) in moderate yield and high di-

Scheme 1