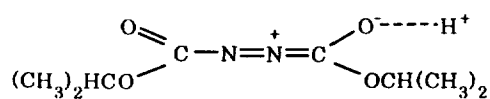


Scheme 1.



Scheme 2.

pyrroles is considered initially to form a zwitterionic intermediate I (Scheme 1). An  $\alpha$  hydrogen may then be transferred intramolecularly through a six-membered transition state in the aprotic solvent as shown in Scheme 1. The facile solvation or intermolecular protonation by the protic solvent may be an explanation for the better yield. Thus, in protic solvents, it is proposed that the protonated DIPADC (Scheme 2) formed by protonation carbonyl of oxygen of DIPADC facilitates nucleophilic attack of  $\pi$  electron of the pyrrole ring

## Experimental Section

Melting points were determined on a Büchi 510 capillary melting point apparatus and uncorrected. Infrared spectra were recorded on a Perkin-Elmer 683 spectrophotometer. Ultraviolet and visible spectra were recorded on a Shimadzu double-beam spectrophotometer. NMR spectra were recorded on a Varian EM 360-A spectrometer in  $\text{CDCl}_3$  containing  $\text{Me}_4\text{Si}$  as an internal reference. Mass spectra were obtained by using a Finnigan model 3300 mass spectrometer.

**Starting materials.** DIPADC was distilled before use. 1-Phenylpyrroles were prepared by literature methods.<sup>7,8,9</sup>

A typical method of preparation of the adducts in ether: 2-(*N,N'*-Diisopropoxycarbonylhydrazinyl)-1-(*p*-chlorophenyl)pyrrole (2d) and 2,5-bis-(*N,N'*-diisopropoxycarbonylhydrazinyl)-1-(*p*-chlorophenyl)pyrrole (3d). A solution of 1-(*p*-chlorophenyl)pyrrole (0.53g, 3mmole) and DIPADC (1.2g 6 mmole) in anhydrous ether (10ml) was refluxed for 80 h. The solvent was removed by evaporation, and the sticky oil was chromatographed. Purification of the residue by flash chromatography with Hexane : EtOAc (20 : 1) as eluent provided 0.27g (16%) of 1:1 adduct (2d) and 0.33g (20%) of 1:2 adduct (3d): (2d) IR (KBr) 3380 (NH), 2960, 2910, 1740 (C=O), 1690, 1490, 1360, 1310, 1240, 1090  $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  1.2 (dt, 1.2H,  $J=7$  Hz, C- $\text{CH}_3$ ), 4.9 (dq, 2H, OCH), 6.3 (dd, 1H, pyrrole C<sub>4</sub>H), 6.4-6.5 (d, 1H, pyrrole C<sub>3</sub>H), 6.7

(d, 1H, pyrrole C<sub>5</sub>H), 7.2 (dd, phenyl 4H); UV(MeOH) 248.5 nm ( $\epsilon=17840$ ). (3d) IR (KBr), 3300 (NH), 2990, 2970, 1740 and 1720 (C=O), 1500, 1380, 1310, 1240, 1100  $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  1.2 (dt, 24H,  $J=7$ Hz, C- $\text{CH}_3$ ), 4.9 (dq, 4H, OCH), 6.3 (s, 2H, pyrrole C<sub>3</sub>H, C<sub>4</sub>H), 6.8 (s, 2H, NH), 7.2-7.4 (m, phenyl 4H); UV (MeOH) 248.5nm ( $\epsilon=17110$ ); mass spectrum,  $m/e$  (%) 581 (43,  $m^+$ )

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## Photoinitiated Polymerization of Acrylic acid Derivatives in Methanol

Hyoung-Ryun Park\*, Yun-Gil Chung, and Heui-Suk Ham

Department of Chemistry, Chonnam National University,  
Kwang-ju 500-757

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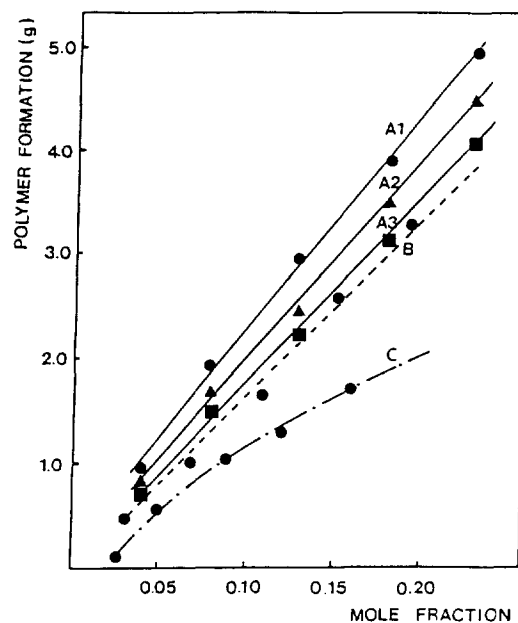
A free radical polymerization by irradiation of UV light has advantages of both simple treatment of a reaction and saving energy using the solar radiation at horizontal surfaces. Particularly, the production process of surface coatings by polymerization of low molecular weight materials under the influence of UV light has been received a growing attention in industry. Studies on the photopolymerization using benzoin ether derivatives as a photoinitiator have extensively been made<sup>1-9</sup>. However, to our knowledge, the quantitative investigation of the photoinitiated polymerization of acrylic

acid derivatives using monochromatic UV light has not been reported to date.

The purpose of this investigation is to understand not only the ability of the photopolymerization of the aromatic carbonyl compounds as a photoinitiator but also the reason of this ability on the basis of the reaction mechanism which has been proposed for the initial process of electronically excited aromatic carbonyl compounds.

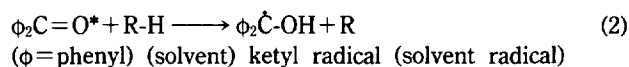
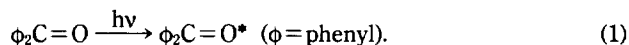
Acrylic acid (AA), methacrylic acid (MA) and methyl methacrylate (MMA) purchased from Junsei Co., Japan were distilled under the reduced pressure after washing with 10% aqueous NaOH solution in order to remove the containing inhibitor. Benzophenone (Merck) was recrystallized from ethanol. Methanol, chloroform and other chemicals (Merck) were used without further purification. Acrylic acid derivatives containing benzophenone (BP), benzoin *iso*-butylether (BIE) or bezoin ethylether (BEE) were dissolved in the deoxygenated methanol. A 15 ml of the solution in a quartz tube was purged for about 5 min. with high purity argon. The solution was then irradiated in a Rayonet photochemical reactor (model RPR-208) equipped with RUL UV lamp as a UV light source ( $\lambda=300$  nm). The intensity of the lamp was measured by potassium ferrioxalate actinometry<sup>11,12</sup>. The reduction yield from  $\text{Fe}_{\text{aq}}^{3+}$  to  $\text{Fe}_{\text{aq}}^{2+}$  after irradiation of air-free aqueous potassium ferrioxalate solution was measured by spectrophotometric method. The lamp intensity was found to be  $9.15 \times 10^{18} \text{ hv} \cdot \text{ml}^{-1} \cdot \text{min}^{-1}$  from the known quantum yield (1.22)<sup>11,12</sup> of  $\text{Fe}_{\text{aq}}^{2+}$ . The irradiated solutions of AA, MA, and MMA were poured into chloroform (30 ml), ethyl ether, and methanol, respectively. The precipitated polymers were filtered, dried under vacuum, and then weighed. The photoproducts were characterized by IR and <sup>1</sup>H-NMR spectroscopy. The IR spectra of the photoproducts which were turned into film form were obtained through IR spectroscopy. The spectrum of the polyacrylate showed a strong, broad band in the range of 3100-3600  $\text{cm}^{-1}$  due to O-H stretching and a strong, sharp band at 1720  $\text{cm}^{-1}$  due to C=O stretching as well as  $\text{CH}_2$  bending vibration at 1450  $\text{cm}^{-1}$  and  $\text{CH}_2$  wagging vibration at 1380  $\text{cm}^{-1}$ . The vibration of the C-O group seemed to be responsible for the absorption band at 1240  $\text{cm}^{-1}$ . The absorption band at 1650  $\text{cm}^{-1}$  due to polymer backbone -C=C- vibration disappeared. The other polymers also showed their characteristic peaks, but the signal due to -C=C- vibration was not observed. <sup>1</sup>H-NMR spectra (at 100 MHz) of a 10-15% (w/v) solution of polymer in  $\text{CDCl}_3$  or  $\text{DMSO-d}_6$  were obtained relative to TMS as an internal standard. The <sup>1</sup>H-NMR spectrum of the polyacrylate exhibited a broad envelope with maxima at  $\delta=1.52$  and  $\delta=2.18$  which were assigned to the  $\text{CH}_2$  and CH protons, respectively. The presence of a band at  $\delta=3.35$  was attributable to the presence of  $\text{OCH}_3$  protons of the methylacrylate units.

The UV spectra of AA, MA, MMA, BP, BIE and BEE in methanol were recorded on UV-spectrophotometer (Hitachi model 557). Acrylic acid derivatives did not absorb the light at 300 nm. The molar extinction coefficient ( $\epsilon$ ) obtained for BP, BIE and BEE were 520.7, 349.3 and 407  $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$  respectively. These results indicate that the photopolymerization begins with absorption of the light by aromatic carbonyl compounds. When the polymers were obtained by irradiation of UV light ( $\lambda=300$  nm) with an intensity of  $1.10 \times 10^{21} \text{ hv} \cdot \text{ml}^{-1}$  ( $\lambda=300$  nm) to the monomer/methanol mixture



**Figure 1.** Polymer formation after irradiation ( $7.82 \times 10^{20} \text{ hv} \cdot \text{ml}^{-1}$ ) of acrylic acid derivatives ( $\bullet$  = acrylic acid;  $\blacktriangle$  = methacrylic acid;  $\blacksquare$  = methylmethacrylate) in methanol with  $5 \times 10^{-3} \text{ M}$  photoinitiator (A; BEE, B; BIE, C; BP) as a function of monomer concentration.

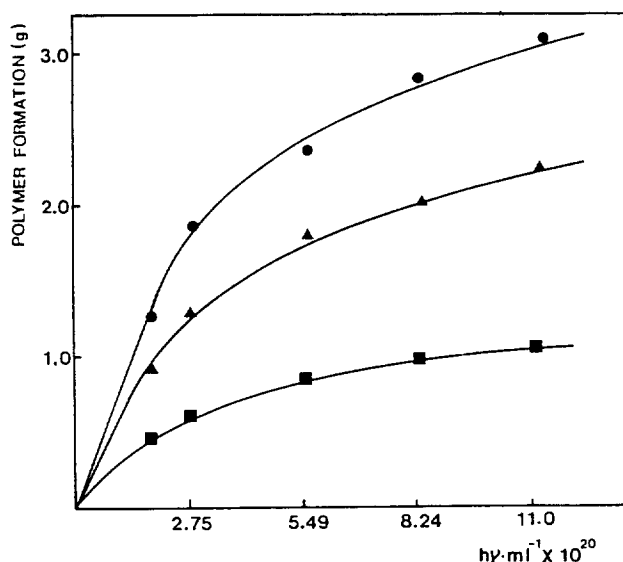
res (2 : 13 v/v) containing BP as a photoinitiator, the obtained polymer yield depended on the concentration of benzophenone up to  $5 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$  and above this concentration the polymer yield was not increased. This behavior is quite similar to the case of the other two photoinitiators. Benzoin ethyl ether was found to be the best initiator among them, as shown in Figure 1. The polymer yield followed the order BEE > BIE > BP and depended on the initial concentration of monomers. Furthermore, the polyacrylate was produced more than the other two polymers (AA > MA > MMA) under the same initial concentration of photoinitiators, and their photopolymerization depended on the number of quanta as well as on the initial concentration of monomers. This is also true for the case of copolymers. The copolymerization of AA and MA gave higher yield than the other two cases (MA and MMA, AA and MMA) under the same experimental conditions. The initial quantum yields of the obtained polymers are summarized in Table 1. Although the molar extinction coefficient of BP had the greatest value among the applied photoinitiators, the polymerization was produced the lowest yield. The polymerization appears to be affected by molecular structure rather than the molar extinction coefficient. The initial process of electronic excitation of aromatic carbonyl compounds has not been completely understood. Nevertheless, it is generally accepted that the electronically excited benzophenone is converted to ketyl radical by abstracting a hydrogen atom from either monomer or solvent. In the contrast, other aromatic carbonyl compounds split directly into benzoyl, and benzyl or alkyl free radical<sup>12,13</sup>.



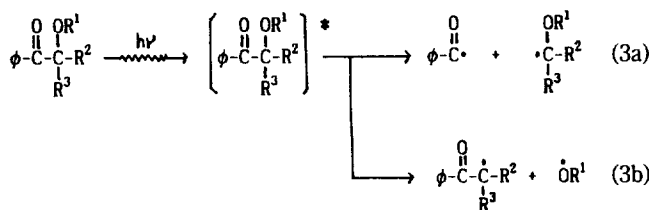
**Table 1.** The initial quantum yield ( $Q_i$ ) of the obtained polymer by the irradiation ( $\lambda=300$  nm) of air-free acrylic acid derivatives in methanol containing  $5 \times 10^{-3}$  M photoinitiator<sup>a</sup>

Monomer ( $X_{monomer}$ )	Photoinitiator ( $5 \times 10^{-3}$ M)		
	BEE	BIE	BP
AA (0.08)	8.34	6.18	4.67
MA (0.08)	2.21	1.83	1.45
MMA (0.08)	1.37	1.13	0.93
AA (0.04)+MA (0.04)	1.34	1.05	0.88
AA (0.04)+MMA (0.04)	0.43	0.35	0.24
MA (0.04)+MMA (0.04)	0.31	0.26	0.15

<sup>a</sup>The initial quantum yield of the copolymers was calculated on the assumption that copolymerizations were carried out by the 1:1 combination of monomers.



**Figure 2.** Polymer formation of acrylic acid in methanol with  $5 \times 10^{-3}$  M benzophenone as a function of the number of quanta. Mole fractions of acrylic acid are 0.129 (●), 0.084 (▲), and 0.041 (■).



This primary reaction of excited aromatic carbonyl compound could explain the relatively low polymer yield in the case of benzophenone. Since the size of ketyl radical in equation (1) is larger than the radicals of BE and BIE produced according to equation (3), it seems that it is more difficult for the ketyl radical to attack  $C_1$  position (the first carbon atom) in monomer ( $\text{CH}_2=\text{CR-COOR}'$ , R and R' = H or  $\text{CH}_3$ ) than the other radicals. Besides, the high polymer yield in the case of AA compared with MA and MMA under the same conditions might support the influence of steric hindre-

nce.

The polymer yield as a function of number of quanta is shown in Figure 2. The polymer yield decreased with the number of quanta. One should note that a back reaction occurred in the system; the obtained polymer was decomposed by the direct photolysis of polymer or by an attack of the radicals which were formed during the photochemical reaction.

In conclusion, polymer yields were found to be dependent on the bulk of the primary radicals which were produced by the electronically excited photoinitiators, and the ability of photopolymerization was affected by the molecular structure of monomers.

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## Cleavage of *m*-Nitrophenyl Acetate in Ethylenediaminated and Diethylenetriaminated $\beta$ -Cyclodextrin Media

Kwanghee Koh Park\*, Jin Pyo Lee, and Joon Woo Park†

*Department of Chemistry, Chungnam National University, Taejeon 305-764*

*†Department of Chemistry, Ewha Womans University, Seoul 120-750*

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Cyclodextrins are cyclic oligosaccharides which possess a hydrophobic cavity. They have attracted great attention as enzyme mimics because of their ability to form inclusion complexes with a variety of substrates and large kinetic ef-