

for the OGE measurement to get even better quality signals.¹⁷

Conclusions

We have studied laser induced impedance changes obtained with a Ti hollow cathode lamps. We were able to acquire big OG signals from Ti lines with high intensity pulsed lasers. In addition to narrow peaks, the spectral profile showed a broad background and additional lines that may have been caused by such things as two-photon transitions by discharge gas and atoms, a photoelectric effect from the cathode surface, photoionization, a wide spectral laser bandwidth, and laser power broadening of the atomic transitions. The development of optogalvanic spectroscopy as a potential analytical technique requires that these problems be solved.

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Photo-Crosslinking of Poly (glycidyl methacrylate) Initiated by N-Hydroxyphthalimide Sulfonates

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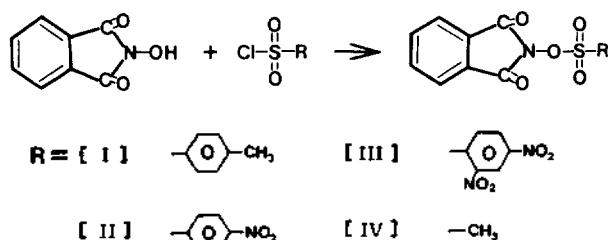
The photoacid generation efficiency of four N-hydroxyphthalimide sulfonate derivatives was studied by photo-crosslinking reaction of poly (glycidyl methacrylate) in solid film state. The relative photoacid generation efficiency was increased in the order of N-hydroxyphthalimide methanesulfonate > -toluenesulfonate > -nitrobenzenesulfonate > -dinitrobenzenesulfonate, and the reaction was efficiently sensitized by benzophenone suggesting that this photoreactions is likely to proceed through its triplet excited state.

Introduction

Photoinitiators play an essential role in the light induced polymerization process. They are widely used for photocurable coatings, UV inks, paints, printing plates, and adhesives.¹ Photoinitiators can be classified into two types on the basis of the reaction mechanisms *i.e.*, free radical and cationic photoinitiators. Most of the technically applied photochemical

processes are based on free radical photoreactions at present. The cationic photoinitiators, however, have several advantages over radical photoinitiators such as no oxygen inhibition, induction of ring opening polymerization, and no volume contraction during polymerization and it appears that in addition to free radical also cationic photoinitiators will be increasingly applied in the future.²⁻⁵

Crivello *et al.*,⁶⁻⁹ have discovered that onium salts are effi-



Scheme 1.

cient photoinitiators for cationic photopolymerization. Some UV deblockable latent sulfonic acid derivatives as well as onium salts are also developed.¹⁰⁻¹² Most of the known cationic photoinitiators are derivatives of onium salts but they have several disadvantages such as their poor solubility in organic solvents and presence of heavy atoms or toxic elements such as As, Sb, Se, P, S, or halogen limiting their application to industrial or biomedical systems. In this paper, photocross-linking of poly (glycidyl methacrylate) (PGMA) initiated by N-hydroxyphthalimide sulfonate derivatives [I]-[IV] is reported and compared their photoacid generation efficiency at solid film state.

Experimental

Materials. N-Hydroxyphthalimide, toluenesulfonyl chloride, *p*-nitrobenzenesulfonyl chloride, 2,4-dinitrobenzenesulfonyl chloride, methanesulfonyl chloride were purchased from Aldrich Chemical Company and used without further purification. Glycidyl methacrylate was purchased from Fluka and purified by vacuum distillation. Solvents were purified by normal procedure.

Instruments. UV, IR and NMR spectra were recorded on Varian Cary-1 UV-visible spectrophotometer, Mattson Polarix FT-IR spectrophotometer, and JEOL PMX60S_T NMR spectrometer, respectively. Irradiations were carried out in a Rayonet photochemical reactor (The Southern New England Ultraviolet Company) Model RPR-100 or RPR-208 equipped with 254 nm or 300 nm fluorescent lamps.

Synthesis of N-hydroxyphthalimide sulfonate derivatives. To a solution of N-hydroxyphthalimide (0.01 mol) in THF was added NaH (0.1 g) and the solution was stirred at room temperature for 1 hr. Corresponding sulfonyl chloride (0.01 mol) in THF was added to the solution dropwisely and the reaction mixture was stirred at room temperature for 4 hrs. The reaction mixture was filtered to remove salt and the filtrate was evaporated to dryness. The crude product was recrystallized from acetonitrile-water (2:3).

Compound [I]. Yield: 70%; mp. 162°C; UV (CH₃CN): λ_{max} ($\log \epsilon_{\text{max}}$) 294 (4.22); MS (12 eV): *m/e* 91 (100), 132 (5.9), 155 (87), 317 (M⁺, 9.0); IR (KBr): 3067, 2980, 1747, 1595, 1465, 1390, 1182 cm⁻¹; ¹H-NMR (CDCl₃, 60MHz): δ 7.8 (s, 4H), 7.6 (d, 4H), 2.45 (s, 3H).

Compound [II]. Yield: 80%; mp. 182°C; UV (CH₃CN): λ_{max} ($\log \epsilon_{\text{max}}$) 292 (4.52); MS (14 eV): *m/e* 122 (33), 132 (55), 162 (23), 186 (100), 348 (M⁺, 50); IR (KBr): 3107, 1753, 1608, 1537, 1346, 1194 cm⁻¹; ¹H-NMR (CDCl₃, 60MHz): δ 8.4 (q, 4H), 7.9 (s, 4H).

Compound [III]. Yield: 80%; mp. 193°C; UV (CH₃CN): λ_{max} ($\log \epsilon_{\text{max}}$) 296 (4.54); MS (10 eV): *m/e* 146 (31), 162 (13),

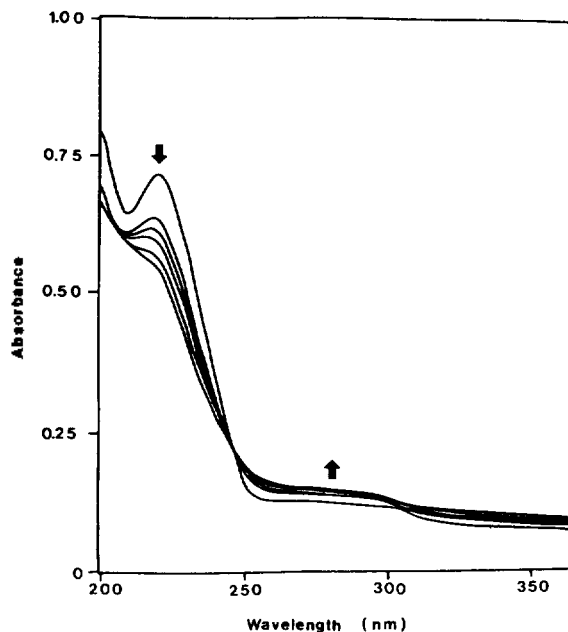


Figure 1. UV spectral changes of the compound [I] in PGMA film with various irradiation time; 0, 5, 10, 20, 40, 60 min. The arrows show the direction of changes in absorbance with irradiation.

231 (100), 393 (M⁺, 8.0); IR (KBr): 3109, 1759, 1606, 1553, 1415, 1344, 1199 cm⁻¹; ¹H-NMR (DMSO-D₆, 60MHz): δ 8.8 (s, 1H), 8.5 (s, 2H), 7.8 (s, 4H).

Compound [IV]. Yield: 55%; mp. 169°C; UV (CH₃CN): λ_{max} ($\log \epsilon_{\text{max}}$) 298 (4.30); MS (10 eV): *m/e* 241 (M⁺); IR (KBr): 3036, 2935, 1737, 1465, 1388, 1184 cm⁻¹; ¹H-NMR (CDCl₃, 60MHz): δ 7.8 (s, 4H), 3.6 (s, 3H).

pH changes of N-hydroxyphthalimide sulfonate solution. 1 × 10⁻⁴ M of N-hydroxyphthalimide sulfonates in acetonitrile-water (2:3, v/v) were irradiated at 254 nm and the pH changes of the solution were monitored. Benzophenone was added to make 1 × 10⁻³ M and 300 nm UV light was irradiated to investigate the triplet sensitizer effect on pH changes.

Synthesis of poly (glycidyl methacrylate) (PGMA). PGMA was prepared by polymerization of glycidyl methacrylate with AIBN as initiator after precipitation in methanol. PGMA sample films were prepared as follows. THF (2.5 ml) solution of PGMA (10%, w/v) containing 2 wt% cationic photoinitiator was coated on polyvinyl acetate film and dried at 70°C. The film (3.5 × 5.5 cm) was irradiated at room temperature with RPR-100 photochemical reactor using merry-go-round apparatus. After irradiation, the film was immersed in THF and insoluble fraction was determined by weighing the residual films.

IR absorbance change measurements. PGMA (10 wt%), sulfonate ester (2 wt%) and with or without benzophenone (2 wt%) was dissolved in THF (2.5 ml) and the solution was spin coated on silicon wafer and dried at 70°C for 10 min. The absorbance change at 3500 cm⁻¹ was observed by FT-IR with time of irradiation at 254 or 300 nm. One module of RPR-208 photochemical reactor was used for this experiment.

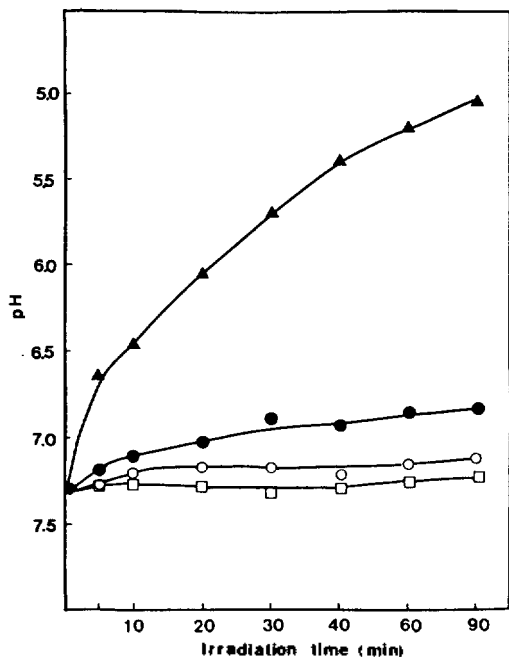


Figure 2. pH changes of N-hydroxyphthalimide sulfonate solutions (1×10^{-4} M in acetonitrile-water) with time of irradiation. (●), compound [I]; (□), [II]; (○), [III]; (▲), [IV].

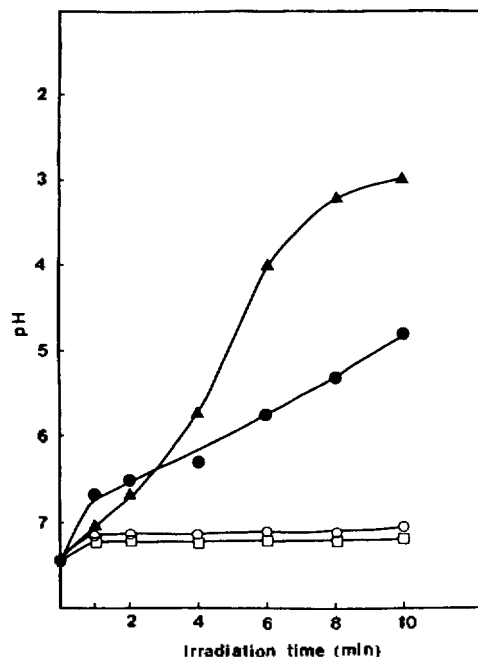


Figure 3. pH changes of N-hydroxyphthalimide sulfonate solutions (1×10^{-4} M in acetonitrile-water) with time of irradiation in the presence of benzophenone (1×10^{-3} M). (●), compound [I]; (□), [II]; (○), [III]; (▲), [IV].

Results and Discussion

N-Hydroxyphthalimide sulfonate derivatives (HPS) are synthesized by the reaction of N-hydroxyphthalimide and sulfonyl chloride in the presence of NaH as a base. Physical and spectral data of the products are summarized at the experimental section. UV spectra of these compounds show ϵ_{max} value of 17,000-34,000 and red shift of absorption maximum with increasing solvent polarity around 290-300 nm indicating (π - π^*) transitions. The change in the absorption spectra of the compound [I] in PGMA film with irradiation time is shown in Figure 1. The absorbance near 220 nm decreased with irradiation time and isosbestic point was observed at 246 nm. A similar result was obtained when other HPS were used. Photolysis of compound [I] in acetonitrile solution yielded *p*-toluenesulfonic acid which was confirmed by HPLC and TLC. On irradiation of UV light, the cleavage of N-O bond of N-hydroxyphthalimide sulfonates, and the subsequent abstraction of hydrogen atoms from solvent or polymer molecules, leads to the formation of toluenesulfonic acid.

The pH changes of HPS in acetonitrile-water (3:5, v/v) solution with time of irradiation at 254 nm are shown in Figure 2. The relative photoacid generation effectiveness was increased in the order of [IV]>[I]>[III]>[II]. Similar results were obtained when benzophenone was used as a photosensitizer as shown in Figure 3, but sensitized photoreaction was far more effective for the photoacid generation.

The photo-crosslinking of PGMA with HPS is shown in Figure 4. The insoluble fraction of PGMA was increased with irradiation time and the effectiveness of photo-crosslinking was in the order of [IV]>[I]>[III]>[II]. The effectiveness of photo-crosslinking of PGMA is in parallel with that of photoacid generation. The IR spectrum of PGMA film con-

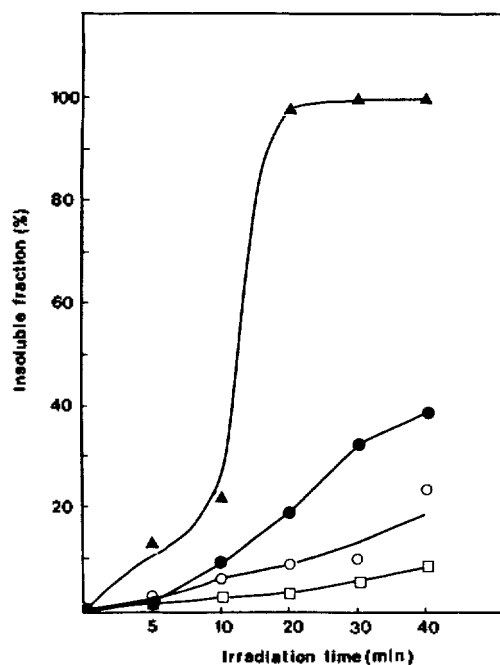


Figure 4. Insoluble fraction of PGMA films with time of irradiation containing four different N-hydroxyphthalimide sulfonates. (●), compound [I]; (□), [II]; (○), [III]; (▲), [IV].

taining the HPS showed gradual increase of hydroxyl groups and decrease of epoxy groups with increase of irradiation time. The results suggest that the photo-crosslinking of PGMA film is caused by the sulfonic acid which is formed *via* photolysis of HPS.

The effectiveness of photoacid generation of HPS in solid

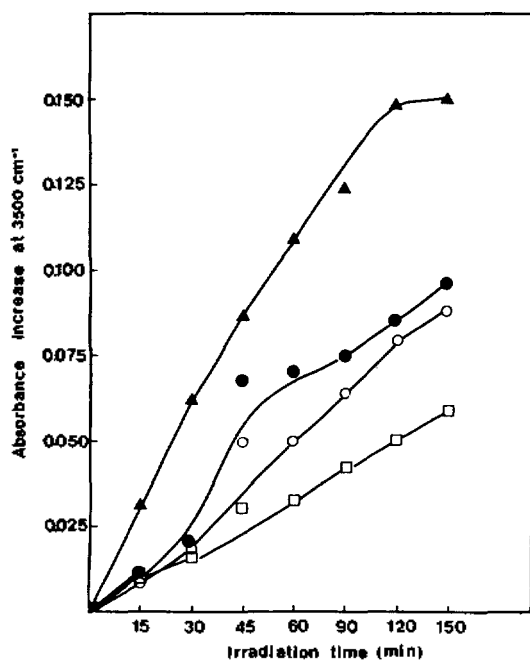


Figure 5. Absorbance increase of PGMA films at 3500 cm^{-1} by irradiation to 254 nm containing four different N-hydroxyphthalimide sulfonates. (●), compound [I]; (□), [II]; (○), [III]; (▲), [IV].

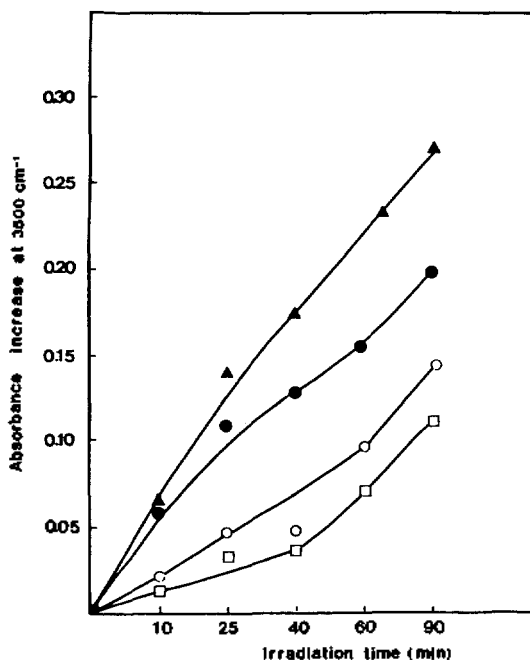


Figure 6. Absorbance increase of PGMA films at 3500 cm^{-1} by irradiation to 310 nm in the presence of benzophenone and four different N-hydroxyphthalimide sulfonates. (●), compound [I]; (□), [II]; (○), [III]; (▲), [IV].

state is also studied by the IR absorbance changes of hydroxyl group of PGMA film. Figure 5 shows the absorbance change of PGMA film at 3500 cm^{-1} with time of irradiation for four HPS. The order of relative absorbance increase was [IV] > [I] > [III] > [II]. Same order was obtained when ben-

Table 1. UV, DSC Data for N-Hydroxyphthalimide Sulfonate Ester Derivatives

Compound	UV λ_{max} (log ϵ_{max})	T_m ($^{\circ}\text{C}$)	T_d ($^{\circ}\text{C}$)
[I]	220 (4.71), 294 (4.22)	162	274
[II]	218 (4.63), 292 (4.52)	182	264
[III]	220 (4.76), 296 (4.54)	193	246
[IV]	225 (4.75), 298 (4.30)	169	290

T_m is the melting point.

T_d is the temperature of onset of decomposition.

zophenone was used as a photosensitizer with higher efficiency.

All the results shown above revealed that the N-hydroxyphthalimide methane or toluenesulfonates ([IV] or [I]) show a higher photoacid generation efficiency than the N-hydroxyphthalimide nitrobenzenesulfonates ([II] or [III]). Photolysis of HPS lead to homolytic cleavage of the N-O bond giving a radical pair consisting of phthalimidyl radical and sulfonyl radical. The pair can either collapse to regenerate the starting HPS or it can undergo cage escape and hydrogen abstraction gives sulfonic acid and N-hydroxyphthalimide. Photolysis of compound [II] or [III] containing electron withdrawing groups gives more electron deficient sulfonyl radical than compound [IV] or [I], and it has higher probability of collapse to regenerate the starting compounds than that of cage escape.

In the presence of benzophenone, the energy transfer from benzophenone to HPS leads to decompose homolytically to give phthalimidyl radical and sulfonyl radical. As in the mechanism for direct photolysis, the sulfonyl radical abstract a hydrogen atom from the medium to give a sulfonic acid. The photoacid generation efficiency of HPS increased efficiently in the presence of benzophenone suggesting that this photoreaction is likely to proceed through its triplet excited state.

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Carbonylation of (Dichloromethyl)benzene Catalyzed by Cobalt Carbonyl and Iron Carbonyl under Phase Transfer Catalysis

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Treatment of (dichloromethyl)benzenes with CO (1 atm) in the presence of catalytic amount of $\text{Co}_2(\text{CO})_8$, $\text{Fe}(\text{CO})_5$, and BTEAC under two phase systems with $\text{NaOH}(\text{aq})$ and PhCH_3 containing small amount of alcohol for 20 hours at 80°C gives phenylacetic acids in moderate yields.

Introduction

It is only after 1976¹ that organotransition metal anions are first employed in phase transfer catalysis, and since then they have made an exponential growth in this area. One advantage of using these transition metal complexes is that such reactions which would not otherwise occur, can be affected by these complexes under mild reaction conditions. The organotransition metal catalyzed carbonylation is one of such examples.

Benzyl halides have been extensively studied using cobalt²⁻⁹, iron¹⁰⁻¹², nickel¹³⁻¹⁹ and palladium²⁰ in phase transfer catalysis. For example, Alper reported that benzyl chlorides and bromides reacted with carbon monoxide in the presence of dicobalt octacarbonyl under phase transfer catalysis at room temperature to give phenylacetic acids in good yields.^{21,22} Brunet *et al.*^{23,24} reported that the cobalt carbonyl catalyzed carbonylation of aryl and vinyl halides gave benzoic acid and propenoic acid, respectively, in excellent yields in the presence of photostimulated phase transfer catalyst. Recently they also²⁵ reported that the carbonylation of iodobenzene was catalyzed by bimetallic $\text{Co}_2(\text{CO})_8/\text{Fe}(\text{CO})_5$ catalysts in the presence of Bu_4NBr in a two phase system to give benzoic acid, benzophenone, and biphenyl. However, bromobenzene did not react with the above bimetallic system.

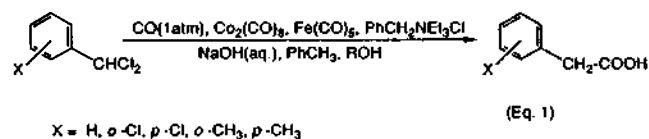
Despite a great amount of research on the phase transfer catalyzed carbonylation, little attention has been paid to catalytic carbonylation of organic geminal halides by transition metal complexes.²⁶⁻²⁹

In the course of our investigation for the carbonylation of (dibromomethyl)benzenes³⁰, YArCHBr_2 under phase transfer catalysis, we found that carbonylation of (dichloromethyl)benzene did not occur. Accordingly this paper deals with simple and convenient carbonylation of (dichloromethyl)benzenes using bimetallic system of $\text{Co}_2(\text{CO})_8$ and $\text{Fe}(\text{CO})_5$ under phase transfer catalysis by modification of the reaction con-

ditions.

Results and Discussion

In the case of phase transfer catalysis, the carbonylation of (dibromomethyl)benzenes to phenylacetic acids takes place successfully under the mild conditions (1 atm of CO, r.t.). But, (dichloromethyl)benzene can not be converted to phenylacetic acid and remains as a reactant. Treatment of (dichloromethyl)benzenes with carbon monoxide in the presence of catalytic amounts of $\text{Co}_2(\text{CO})_8$, $\text{Fe}(\text{CO})_5$, and PTC in a two phase system composed of $\text{NaOH}(\text{aq})/\text{C}_6\text{H}_5\text{CH}_3$ containing a small amount of alcohol for 20 hours at 80°C gives the corresponding carboxylic acids in moderate yields (Eq. 1).



After the reaction, organic phase contains unreacted (dichloromethyl)benzene and small amount of 1,2-diphenylethane. But, the focus is paid to the aqueous phase containing carboxylic acids. The optimum yield is pursued under the conditions given at the footnote of Table 1 by controlling the reaction time from 5 to 20 hours; the yields of phenylacetic acid increase gradually with time. But, the longer reaction time than 20 hours does not show change in the yield of the carboxylic acid.

Many alcohols having $\text{C}_1\text{-C}_4$ except *t*-butyl alcohol show similar yields of the carboxylic acids. In the absence of alcohol, the yield of phenylacetic acid is reduced to 30%. Dioxane, di*n*-butyl ether, and *i*-propyl alcohol as the organic phase gave low yield of phenylacetic acid. The higher pressure of carbon monoxide (10 atm) could not improve the yield of phenylacetic acid compared with 1 atm using benzene-ethyl alcohol