Alkyl phenylglyoxylates as radical photoinitiators creating negative photoimages[1]

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Alkyl phenylglyoxylates are shown to be efficient photoinitiators for acrylate polymerization. Benzoyl and phenyl radicals derived from intermolecular hydrogen abstraction are the initiating species. A negative photoimage system was developed based on this observation. The imaging material consists of a polymeric phenylglyoxylate initiator and to-be-crosslinked diacrylate monomers. The contrast and sensitivity of this system have been measured.

In the last two decades, photopolymerization has found an increasing number of applications, most notably in the printing and electronics industries.[2] It is a versatile and widely used route to different UV curable coatings, adhesives and inks. Photopolymerization processes have many advantages over thermal polymerization reactions. The production rates of photopolymers are higher and the processes can be carried out under less demanding conditions.[3]

Almost all commercial photoinitiators are compounds which produce either free radicals and/or acids upon irradiation at appropriate wavelength.[4] The most common are benzoin and its derivatives, acetophenone and its derivatives, aromatic ketone–amine combinations and various onium salts.

Methyl phenylglyoxylate was sold commercially as a photoinitiator many years ago, and we have been interested in understanding the processes by which it initiates polymer-forming processes. The photochemical reactions of alkyl phenylglyoxylates have been studied extensively.[5] Considering the radical species generated in the intermolecular hydrogen abstraction induced radical chain processes (Scheme 1),[5a] we have elucidated the mechanism for phenylglyoxylate initiation of photopolymerization processes.

In our earlier study,[5a] alkyl phenylglyoxylates were found to undergo both intramolecular (Norrish Type II) and intermolecular hydrogen abstraction leading to radical chain reactions in aprotic solvents. The overall process as exemplified by ethyl phenylglyoxylate is shown in Scheme 1.

The intermediate hydroxyphenyl ketene can be trapped by alcohols[5b] and imines[6] or decarbonylate to form benzaldehyde **2** when efficient ketene trapping reagents are absent. Benzoyl radicals are produced by intermolecular hydrogen abstractions by one excited alkyl phenylglyoxylate molecule on the ground state of another like itself. Products resulting from benzoyl radical addition to ground state alkyl phenylglyoxylates, **4**, and subsequent coupling with other radicals, **5**, were also isolated. Biphenyl **6** results from solvent involvement in the hydrogen abstraction process. However, phenyl radicals may also result from a loss of carbon monoxide from benzoyl radical. One or more of these radicals can initiate radical polymerization processes.

Experimental

Materials

Benzene (Aldrich) was dried over sodium benzophenone ketyl under argon. Acrylate monomers and styrene were also obtained from Aldrich. All monomers contain radical inhibitors, typically 10–100 ppm hydroquinone, and were used without further purification. Other chemicals were obtained from commercial sources and used as received. NMR spectra were taken with either a Varian Gemini 200 NMR spectrometer or a Varian Unity Plus 400 NMR spectrometer using $CDCl_3$ as solvent. Chemical shifts are in ppm with $SiMe_4$ as the internal standard; J values in Hz. GC measurements were carried out on a Hewlett-Packard(HP) 5890 Gas Chromatograph with a 30 m × 0.253 mm ID × 0.25 μm film thickness DB-1 column (J & B Scientific) and a flame ionization detector. GC–MS were taken on Hewlett-Packard 5988 mass spectrometer coupled to a HP 5880A GC with a 30 m × 0.25 mm ID × 0.25 μm film thickness DB-5 ms column (J & B Scientific), interfaced to a HP 2623A data processor. Thin layer chromatography was performed with Whatman silica gel coating TLC plates. Silica gel (60 Å, 60–200 mesh) used in column chromatography was from J. T. Baker Chemical Company. High resolution mass spectra were obtained from the University of Illinois at Urbana-Champaign.

Photochemical polymerization

Polymeric thin films were made by exposing 15 μm films of target monomer and alkyl phenylglyoxylate to UV light in a Colight M218 light bath (two 400 W medium-pressure Hg lamps). Fluorescent probe was added when necessary. Monomeric films were made by squeezing a drop of the mixture between two Pyrex glass plates divided by a 15 μm Teflon spacer.

Photochemical reactions in benzene were carried out in Pyrex test tubes. Samples were dissolved in solvent and sealed with a rubber septum bound by sticky parafilm. Degassing was achieved by bubbling dry argon gas through the solution for 10–15 min. Irradiation was carried out in a Rayonet RPR-100 photoreactor equipped with sixteen 350 nm GE F8T5·BLB UV lamps.

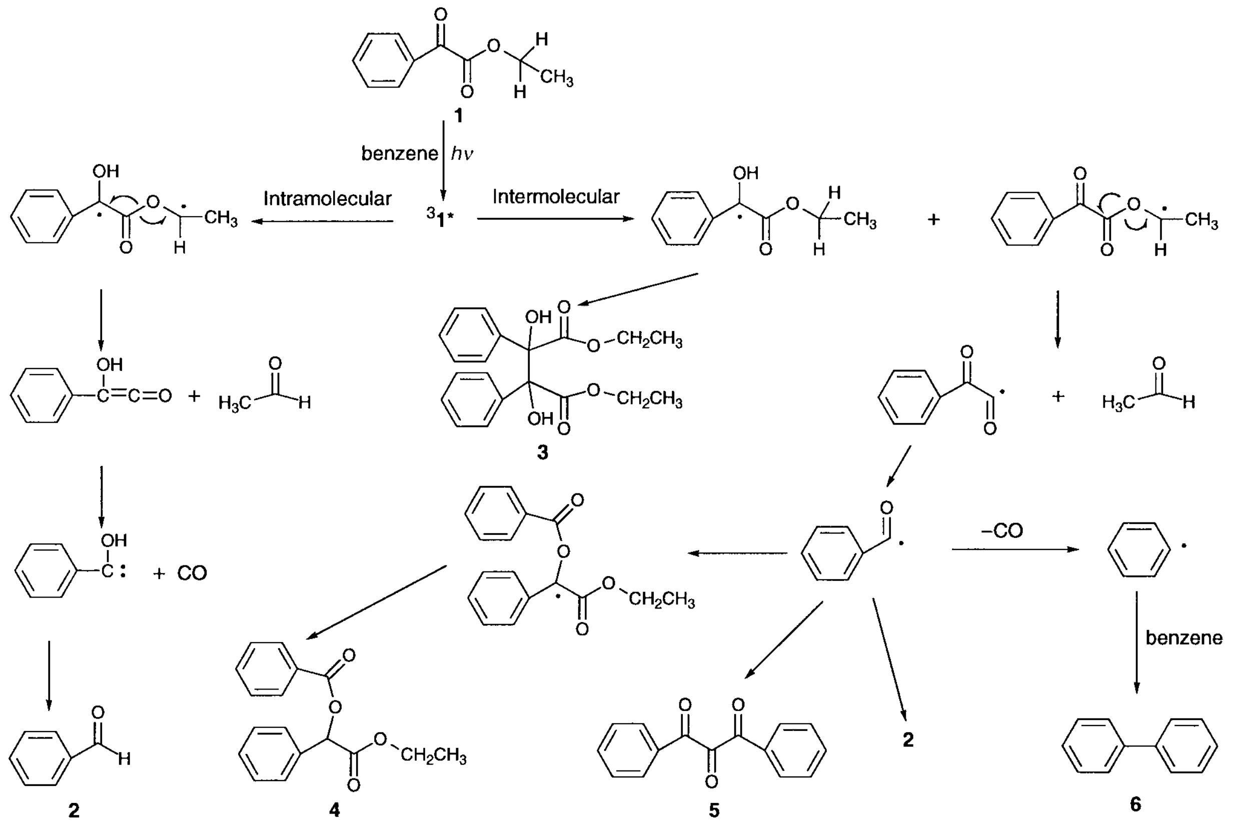
Resist films were prepared by spin coating a 25% (w/w) benzene solution of **9** and **10** (1:4, w/w) at 6000 rpm for 20 s with a Headway Research, Inc. spin-coater onto silicon wafers (Si-tech, Inc.) of appropriate sizes. Irradiations of resist films were performed by defocused UV irradiation from a 200 W high-pressure mercury arc lamp filtered through a 365 nm filter (bandwidth *ca.* 40 nm). The distance from the film to the lamp was fixed at 11 cm. The photon flux from the irradiation source was measured by a Scientech 365 power and energy meter positioned at the same position as the resist films.

Time resolved laser flash photolysis

Nanosecond laser flash photolysis was carried out on a setup described by Ford and Rodgers[7] using the third harmonic of a Q-switched Nd:YAG laser (Continuum, YG660) as excitation source. The sample solution in a quartz cuvette was purged by Argon for 5 min before and during the experiment. The samples were excited with 355 nm pulses (pulse width *ca.* 7 ns).

Ethyl [$^2H_5$]phenyl glyoxylate [$^2H_5$]-1

[$^2H_6$] benzene 0.8 g (10 mmol), 1.4 g (10 mmol) ethyl oxalyl chloride and 25 ml of anhydrous methylene chloride were



Scheme 1

placed in a 50 ml flask equipped with a magnetic stirrer and suspended in an ice–salt bath. After stirring for 10 min, 1.7 g (12 mmol) of aluminium chloride was added in small portions over 10 min. When the solution turned red-brown and became homogeneous, the ice–salt bath was removed and the mixture was poured over 50 g of crushed ice and 30 ml of concentrated hydrochloric acid. The organic layer was washed with 30 ml of 0.1 M sodium hydroxide ($\times$ 3) and water ($\times$ 3). After separating the organic layer and evaporating the solvent, the crude product was purified by column chromatography using hexanes–ethyl acetate (10 : 1) as the eluting solvent. 1.5 g (83%) of pure product was obtained. δ_H (400 MHz, $CDCl_3$), 1.33 (t, *J* 6.8, 3H), 4.36 (q, *J* 6.8, 2H). δ_C (50 MHz, $CDCl_3$), 14.04, 62.26, 128.30 (t), 129.54 (t), 132.21, 134.32 (t), 163.75, 186.33. MS: 54 (11), 82 (31), 110 (100), 155 (2.0), 183 (0.1). HRMS *m/z* 183.0941; calc. 183.0944.

Results

Photopolymerization of dimethacrylates

For practical purposes, photocurable resins consist of a combination of multifunctional acrylates that form complex polymeric networks upon polymerization. For instance, a mixture of di-, tri-, and penta-acrylates is used as standard resin in our group for stereolithography studies.[8] We used pure dimethacrylate monomers in this study to simplify the structures of resulted polymers.

Ethyl phenylglyoxylate (**1**) was tested as the photoinitiator to polymerize various monomers. Generally, 0.5% (by mass *vs.* monomer) of ethyl phenylglyoxylate was dissolved in a benzene solution of the monomer contained in a Pyrex test-tube and the solution was degassed by purging with dry argon for 15 minutes. Irradiation with a medium-pressure mercury lamp (maximum emission 365 nm) converted the monomeric solution to a non-mobile polymer gel. To reveal the efficiency of the initiation, 0.1% (*vs.* monomer) of *N*,*N*-di-*n*-butyl-5-(dimethylamino)naphthalene-1-sulfonamide (DASD) was incorporated as a fluorescent probe,[9] and the progress of polymerization followed with a cure monitor.[10] A typical result for the polymerization of di(ethylene glycol) dimethacrylate is shown in Fig. 1. The ratio of probe fluorescence intensities at 456 and 558 nm indicates the extent of polymerization.

Initiator species

Equal amounts of **1** and methyl acrylate were dissolved in dry benzene and degassed by purging with argon. After irradiation, the major product observed was diethyl 2,3-dihydroxy-2,3-diphenyl succinate **3**. The putative benzoyl and phenyl radical

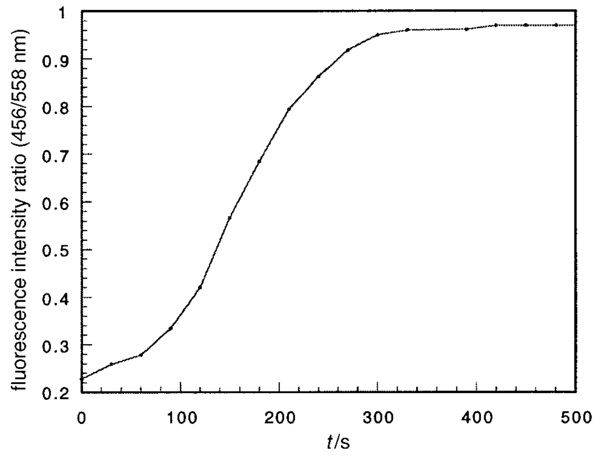
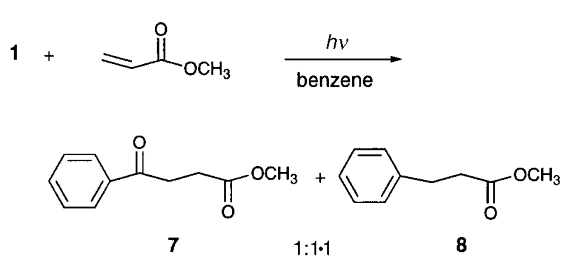
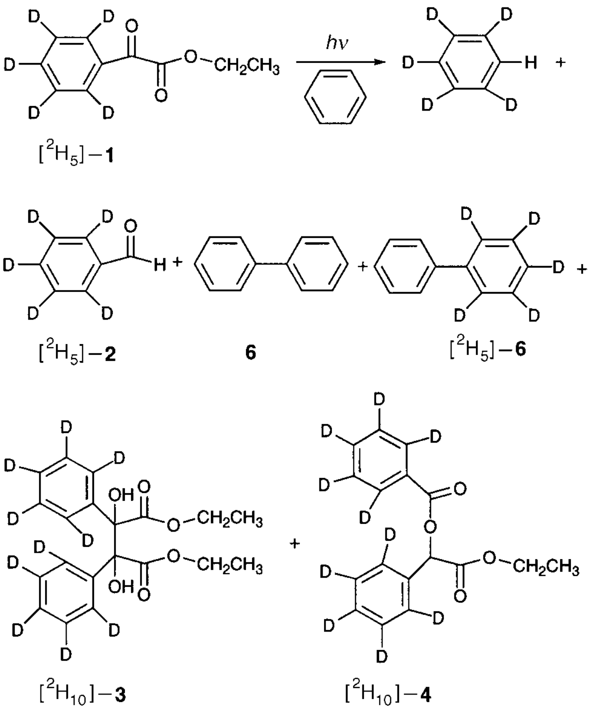


Fig. 1 Ethyl phenylglyoxylate initiated polymerization of di(ethylene glycol) dimethacrylate. The progress of the reaction was monitored by a cure monitor with an added fluorescence probe.



Scheme 2



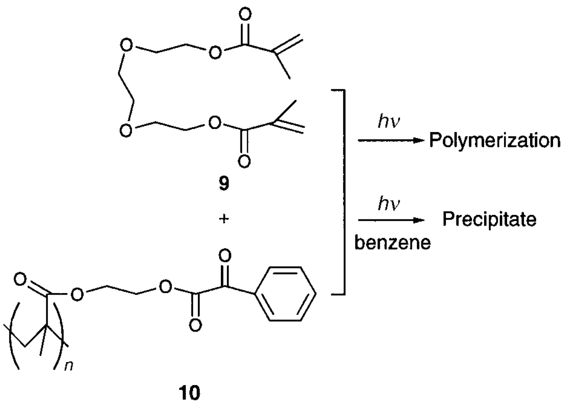
Scheme 3

derived products **2**, **4**, **5** and **6** were not found, but the presence of ethyl 3-benzoylpropionate **7** and methyl 3-phenylpropionate **8** (Scheme 2) was confirmed from comparison of the mass spectral cracking patterns obtained from GC–MS analyses, as well as by comparing their retention times on two different GC columns with authentic samples. The relative quantities of **7** and **8** were assessed by GC analysis with the instrument calibrated using undecane as the added internal standard. The presence of **7** and **8** suggests that both benzoyl radical and phenyl radical initiates the polymerization process.

In order to clarify the origin of the phenyl radical, ethyl pentadeuterophenylglyoxylate ([$^2H_5$]-**1**) was synthesized and photolysed in benzene, Scheme 3. Normal isotopic patterns were observed for compounds [$^2H_5$]-**2**, [$^2H_{10}$]-**3**, [$^2H_{10}$]-**4**. The presence of pentadeuterobenzene and biphenyl with different isotopic patterns (**6** and [$^2H_5$]-**6**) indicates that phenyl radicals are derived from both [$^2H_5$]-**1** and the solvent, benzene. As indicated in Scheme 1, a benzoyl radical decarbonylates forming the phenyl radical, which can abstract a hydrogen from the solvent molecule and produce the solvent-derived phenyl radical.

Negative photoimaging system

Polymeric photoinitiators offer advantages in that they generally have greater reactivity over their monomeric counterparts.[11] We have studied the photochemistry of poly(methacryloylethyl phenylglyoxylate) **10**.[12] We describe its initiation ability herein. (Scheme 4)



Scheme 4

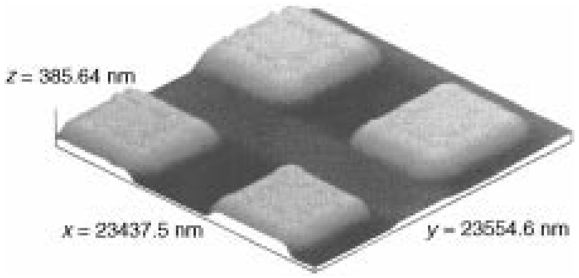


Fig. 2 AFM micrograph of image produced

Irradiation of a benzene solution of **9** and **10** (1:4, w/w) resulted in a precipitate due to the polymerization of **9** initiated by radicals derived from the photolysis of **10**. To exclude the possibility that the precipitate is the result of photoreaction solely of **10**,[12] a neat mixture of **9** and **10** (1:4, w/w) was irradiated. Solidification of the whole mixture was observed due to the polymerization of **9**. An imageable material was derived from a mixture of a multimethylacrylate monomer (**9**) and a polymeric phenylglyoxylate (**10**), that serves as the polymeric free radical photoinitiator. Tri(ethylene glycol) dimethylacrylate (**9**) was chosen as the working monomer since a benzene solution of the mixture of **9** and **10** forms a good film on a silicon surface upon spin coating. A typical negative photoimage produced upon irradiation at a dose larger than the D_i (the insolubilization dose, *vide infra*) is shown in Fig. 2. The image was produced by irradiating a spin

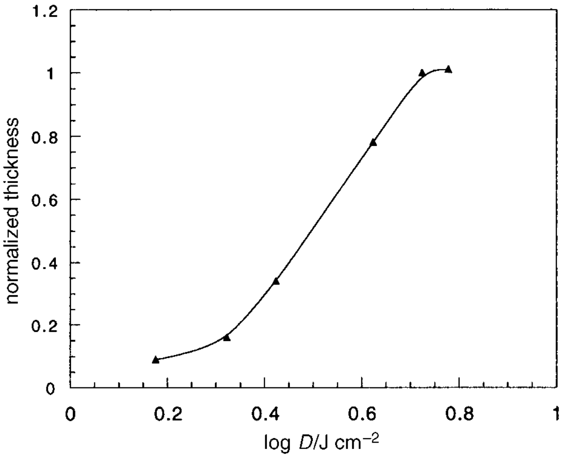


Fig. 3 Sensitivity plot of the negative photoimage

coated film through a TEM T2000-Cu grid with holes of 7.5 × 7.5 µm and bars of 5 µm separating the holes as a soft contact mask. After irradiation, the surface was rinsed with dry benzene for 30 s. The non-irradiated part of the film was totally removed by this development procedure. It is clear that resolution up to 5 µm can be achieved and better resolution could be anticipated with masks having finer structures.

The sensitivity of the photoimage forming process was measured by atomic force microscopy (AFM).[12] The sensitivity curve of this photoimaging system is shown in Fig. 3. The gel dose, D_g (the dose at which the gel makes its first appearance), is about 1.5 J cm^{-2}. The insolubilization dose, D_i, is 6 J cm^{-2}. The sensitivity of the resist, D_s, is defined as the dose required to retain 50% of the original film, and is 3.1 J cm^{-2}.[13] The contrast $\gamma = 1/\log(D_i/D_g)$, is calculated as 1.7. The sensitivity of this photoimage system is higher than the sensitivities of currently employed photoresists (25–200 mJ cm^{-2}), however, the system is of high contrast.[14] Since insolubilization is achieved by the crosslinks of the multiacrylate monomer initiated by photochemically produced radicals, it is expected that the sensitivity of this system could be improved by using monomers with multiacrylic functionalities.

Discussion

Alkyl phenylglyoxylates as photoinitiators for styrene polymerization have also been studied. Although some degree of polymerization was observed, the rate of polymerization is low. The expected adducts of the initiating radicals to styrene, β-phenylpropiophenone (from the benzoyl radical) and bibenzyl (from the phenyl radical) were not observed. The Paternò–Büchi reaction between alkyl phenylglyoxylate and styrene is not expected since the double bond in styrene is not sufficiently electron rich.[15] On the other hand, related alkenes have been shown able to quench excited phenylglyoxylate triplets by electron transfer.[16] The oxidation potential of styrene is 2.22 eV (*vs.* standard calomel electrode, SCE).[17] Taking the reduction potential (−1.227 eV, *vs.* SCE) and triplet energy (66 kcal mol^{-1}; 1 cal = 4.184 J)[16] of methyl phenylglyoxylate, from the Weller equation,[18] eqn. (1),

$$\Delta G_{\mathrm{ET}} = 23.06\,(E_{\mathrm{D}}^{\mathrm{ox}} - E_{\mathrm{A}}^{\mathrm{red}}) - E_{\mathrm{T}} - C \qquad (1)$$

ΔG_{ET}, the free energy change for electron transfer is positive and the electron transfer process is endothermic. However, the triplet energy of styrene is 61.7 kcal mol^{-1},[19] lower than that of a typical alkyl phenylglyoxylate. Energy transfer from the excited triplet state of the alkyl phenylglyoxylate to monomeric styrene is thereby expected. The efficiency of this process is indicated by the rate constant of styrene quenching methyl phenylglyoxylate triplet, 8.0×10^8 dm^3 mol^{-1} s^{-1}, which was obtained by measuring the glyoxylate triplet lifetime in the presence of various concentrations of styrene (Fig. 4).

If triplet reactivity is not hindered by the monomer, alkyl phenylglyoxylates are efficient photoinitiators. The quantum yields of the hydrogen abstraction processes are high,[5a] and these α-keto esters dissolve well in various monomers. Functionalization of both the alkyl[12] and the phenyl[5a] functions of the ester is readily achievable such that initiators designed to fit varying requirements may be constructed.

In conclusion, we have discovered the initiation mechanism for alkyl phenylglyoxylates as photoinitiators for acrylate photopolymerization and successfully employed this chemistry in a negative photoimage system.

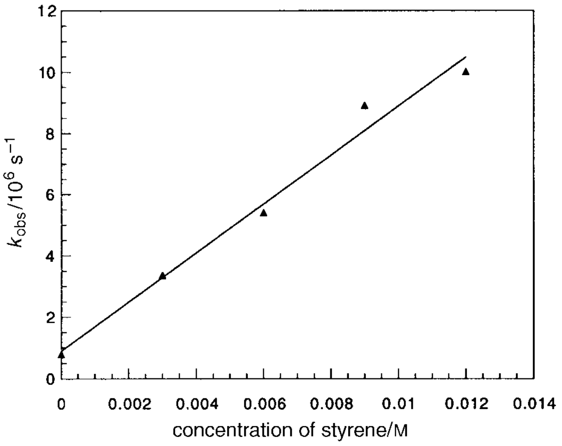


Fig. 4 Decay rate constants of methyl phenylglyoxylate triplet at different styrene concentration

We thank the National Science Foundation (DMR-90113109) and the Office of Naval Research (Navy N00014-91-J-1921) for financial support of this work. The NMR spectrometers were purchased with funds from NSF (CHE9302619), the Ohio Board of Reagents, and Bowling Green State University. We acknowledge their support. Conversations with Dr G. S. Hammond are gratefully acknowledged.

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Paper 7/01797I; *Received* 14*th March*, 1997