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Photochemically Active Polymers Containing Pendant Ethyl Phenylglyoxylate

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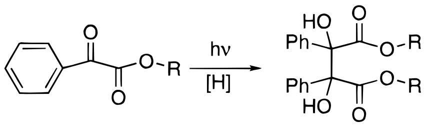
ABSTRACT: Photoreactions of acrylic polymers containing pendant ethyl phenylglyoxylate groups at different distances from the polymeric backbone have been studied. Hydrogen abstraction between pendant groups by an excited triplet phenylglyoxylate carbonyl group from adjacent pendant groups is the primary process. The expected γ-hydrogen abstraction within one pendant group (the Norrish type II reaction) is not observed. The radicals formed react with each other to form cross-linked structures in the polymer. This effects solubility in various solvents which changes significantly after irradiation. The potential of the polymer as an imageable material has been evaluated.

Introduction

In the presence of a hydrogen donor, phenylglyoxylic acid[2] and its alkyl esters[3] undergo bimolecular photoreduction (eq 1) in a manner analogous to benzophenone.[4] In non-hydrogen-donating solvents at low concentration, Norrish type II elimination (eq 2) dominates.[5] Alkyl phenylglyoxylates tend to dimerize in the absence of a hydrogen donor when the concentration of the starting keto ester is high. Under such conditions the alkyl moiety provides the hydrogen source for the photoreduction.[5]



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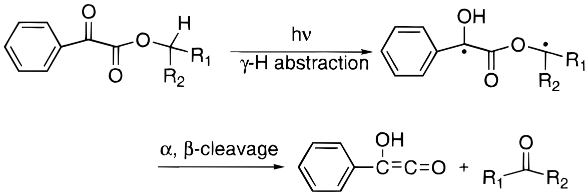

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Polymers containing photoreactive functional groups have been the subject of intensive recent research since they provide for modification of the material to reveal spatially addressable reactive templates on a film surface that could enable combinatorial construction of biologic molecules in a miniature unit area.[6] Polymers having photo-cross-linkable α,β-unsaturated carbonyl functionalities have previously been explored extensively for uses in photolithography[7] and the printing industry.[8] Encouraged by this intensive recent interest in photo-cross-linkable polymers, most of which still derived from α,β-unsaturated carbonyl compounds,[9] we developed polymeric systems from monomers containing novel chromophores with well-studied photoreactivities.

We studied acrylic polymers with pendant ethyl phenylglyoxylate chromophores and found their photoreactivity to be substantially different from that of their monomeric counterparts. Hydrogen abstraction occurs exclusively between pendant functional groups in both neat polymer films and non-hydrogen-donating solvents. Significant solubility changes after irradiation, due to cross-link formation, were observed. The potential of this polymer as an imageable material was evaluated.

Results and Discussion

Syntheses and Solution Photochemistry. Ethyl *p*-2′-methacryloylethylphenylglyoxylate, **1a,** and ethyl *p*-2′-acryloylethylphenylglyoxylate, **1b,** were synthesized, Scheme 1. The corresponding polymers **2a** and **2b** were obtained thermally using 2,2′-azobis(isobutyronitrile) (AIBN) to initiate polymerization. The same procedure was used in an attempt to synthesize ethyl *p*-acryloylmethylphenylglyoxylate, **1c**, though this monomer could not be isolated. Instead, the corresponding polymer **2c** was obtained. Compound **1c** is apparently prone to *in situ* polymerization initiated by the Lewis acids present in the reaction mixture.

Irradiation (~365 nm) of polymer **2a** in benzene (0.02 M, with respect to the phenylglyoxylate chromophore) produced a white precipitate as the only photoproduct, and this was collected by filtration and washed with benzene. Elemental analysis of the precipitate showed the same elemental composition as the starting polymer **2a**. The filtrate, analyzed using gas chromatography (GC), gas chromatography/mass spectrometry (GC/MS) and thin-layer chromatography (TLC), revealed no other photoproducts. Similar results were obtained when **2b** and **2c** were irradiated in benzene. Irradiation of benzene solutions (0.02 M) of monomers **1a** and **1b** also produced only white precipitates. No substantial volatile photoproducts were detected by GC and GC/MS. Since we have previously demonstrated that radicals derived from photoreactions of ethyl phenylglyoxylate efficiently initiate the polymerization of acrylic monomers,[10] it is proposed that radicals resulting from photolysis of **1** (**a, b**) rapidly initiate polymerization of the monomer giving **2** (**a, b**). The precipitate results from secondary reactions of **2** (**a, b**) analogous to that observed when the benzene solutions of the polymer were irradiated (*vide supra*).

Mechanism. When irradiated, the phenylglyoxylate chromophore is promoted to its excited triplet state *via* the singlet manifold, and these have previously been shown to undergo γ-hydrogen abstraction (Norrish type II, eq 2) with a rate constant of 6.4×10^5 s^{-1}.[5] The absence of the expected products indicates that the

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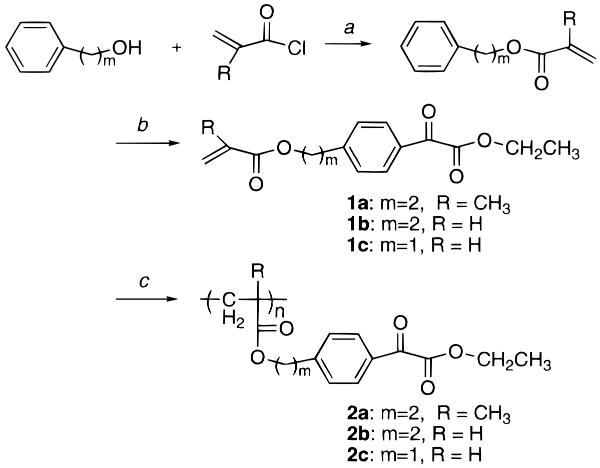
Scheme 1



a) TEA, chloroform, r. t. *b*) AlCl$_3$, ethyl oxalyl chloride, 0°C. *c*) AIBN, benzene, reflux.

Norrish type II process does not occur in polymer **2**. On the other hand, γ-hydrogens of the neighboring pendant group seem readily available for abstraction by the excited carbonyl group based on the observed intermolecular hydrogen abstraction reactions in cases of simple alkyl phenylglyoxylates.[5] Hydrogens α to phenyl rings in the pendant groups are also accessible for abstraction giving rise to a resulting benzyl radical. Other hydrogens in the pendant groups and the polymer backbone are not reactive. The fact that the excited carbonyl group abstracts reactive hydrogen from neighboring groups rather than γ-hydrogen in the same pendant group was initially surprising. This is rationalized due to (1) the inherent low rate of the Norrish type II process of the phenylglyoxylate chromophore due to its unfavorable conformation for intramolecular γ-hydrogen abstraction[11] and (2) hydrogens from other pendant groups in **2** being easily accessed compared to those in a monomeric reaction because the pendant groups in **2** are linked by a polymeric backbone. The mechanism is shown in Scheme 2.

Two sets of radical pairs result from the hydrogen abstraction processes. Abstraction of the γ-hydrogen forms a ketyl radical and an alkyl radical while involvement of the benzyl hydrogen leads to a ketyl radical and a benzyl radical. The radical pairs so produced couple forming substructures **A** and **B**. Because radical centers in the two kinds of radical pairs are stabilized by substituents, these are expected to be sufficiently long-lived to be able to diffuse apart. The separated radicals can couple with each other forming substructures **C**, **D**, and **E**. Since there remain reactive chromophores in substructures **A**, **B**, **D**, and **E**, these can be activated by light to undergo further reactions.

Spectroscopic Evidence. Polymer films prepared by spin coating solutions of **2b** were chosen to obtain spectroscopic evidence for the proposed mechanism. The UV absorption of a film on a glass slide was measured before and after irradiation. A significant decrease in the absorption at 324 nm was observed in agreement with the consumption of the keto carbonyl group. Characteristic changes in infrared spectra were detected when a film on silicon wafer was subjected to irradiation, Figure 1. Before irradiation, the peaks at 1686.30 cm^{-1} (a) and 1736.47 cm^{-1} (b) are attributed respectively to the keto and the ester carbonyl groups of the phenylglyoxylate chromophore. The peak of the acrylic ester carbonyl group overlaps with that of the phenylglyoxylate ester group. During irradiation, the intensity of the keto carbonyl signal decreases and a new broad peak at around 3500 cm^{-1} (c) appears. Irradiation was ceased when the keto group signal could no longer be detected. At this time a single peak at 1728.75 cm^{-1} (d) remains in the carbonyl region of the spectrum, and this is assigned to the nonconjugated carbonyl groups of the polymerized acrylate ester portion and the newly formed α-hydroxyl esters derived from the coupling of the ketyl radicals.

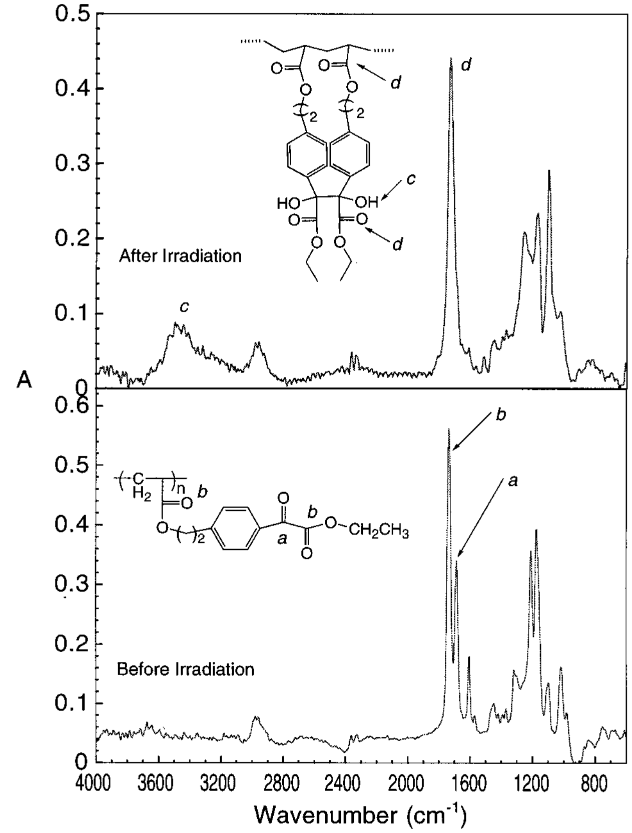


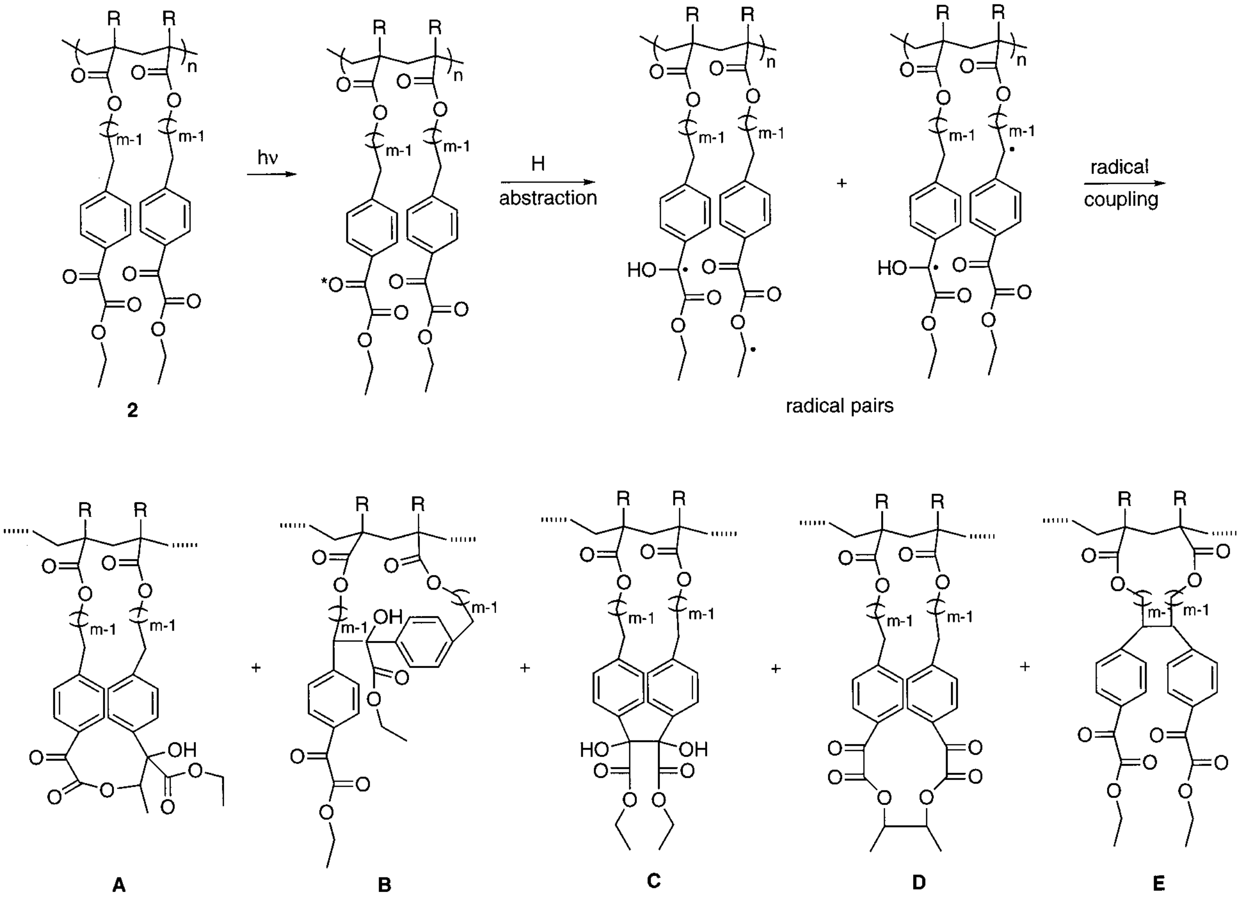
Figure 1. IR spectra of a film of **2b** on silicon wafer before and after irradiation.

The shift of the ester carbonyl signal of the reacting phenylglyoxylate from 1736.47 to 1728.75 cm^{-1} reflects a change in its electronic environment resulting from the conversion of the α-keto group formerly in conjugation to an α-hydroxyl group that does not contribute significantly to delocalization. The presence of hydroxyl groups in the irradiated polymer is further supported by the characteristic broad peak at around 3500 cm^{-1}.

The ^{13}C NMR of **2b** was recorded in deuterated benzene using the APT (Attached Proton Test) sequence, Figure 2a. The keto and the ester carbonyl signals in the pendant phenylglyoxylate are at 186.43 and 164.41 ppm, respectively, in agreement with those of the monomeric α-keto esters.[5] The nonconjugated ester carbonyl derived from the former acrylic group appears at 174.59 ppm.

The cross-linked polymer resulting from irradiation of **2b** in benzene is not soluble in common organic solvents. Its ^{13}C NMR spectrum shown in Figure 2b was recorded in solid state using a sequence adopted in our group for the study of the structures of cross-linked polymers.[12] After irradiation, only two different ester carbonyl carbon signals (176.02 and 166.34 ppm)

Scheme 2



remain. The disappearance of the keto carbonyl carbon signal in the cross-linked polymer indicates that the reactive carbonyl groups are consumed when **2b** was irradiated in solution. The signal at 70.75 ppm is significantly downfield compared to other alkyl carbon signals before irradiation. This signal (70.75 ppm) is assigned to the quaternary carbons that are directly connected to the hydroxyl group.

Laser Flash Photolysis. Transient absorptions were detected when a benzene solution of **2a** (2.0 mg/ml) was subjected to laser flash photolysis at 355 nm, Figure 3. The decay trace monitored at 440 nm is best fitted into a faster exponential decay followed by a slower one. The first component is attributed to the triplet state of phenylglyoxylate and the second to ketyl radical in accordance with the previous study.[5] Similar results were obtained for **2c**. The lifetimes of the transients are collected in Table 1 together with those of a compound previously studied, poly(methacryloylethyl phenylglyoxylate) **3**.[13] The triplet lifetimes of **2a** and **2c** are similar to those of the monomeric phenylglyoxylate while the lifetimes of the ketyl radicals are much shorter than that of the monomeric ketyl radical (~ 80 μs).[5] We attribute this to the radicals produced by hydrogen abstraction between pendant groups in **2** being in proximity because of their common backbone. They are thus more easily deactivated and form coupled products.

Photoreactivity in Film. The photoreactivity of **2** presented an opportunity to utilize this polymer as a single-component negative photoimaging material. Thin films of polymer **2a** and **2c** were prepared by spin-coating benzene solutions onto silicon wafers. After selective irradiation through a mask, sufficient solubility differentiation was achieved to obtain an image. The nonirradiated portions of the film can be dissolved away from the silicon surface by immersing the film in benzene[14] for 1 min. The irradiated portions of the film remain on the wafer.

The sensitivity of this polymer as an imaging material was measured. Films of uniform thickness (~200 nm)[15] were subjected to different doses of light through a TEM2000-Cu grid[16] which served as a soft contact mask. After development, the thickness of the irradiated portions of the film was measured by atomic force microscopy (AFM). A representative AFM micrograph obtained with light of the insolubilization dosage is shown in Figure 4. For each light dosage, the remaining film thickness was measured three times and the results were averaged. A sensitivity curve was constructed by plotting the normalized film thickness against the irradiating dosage as shown in Figure 5 for **2a**.

The sensitivities of the material defined as the dose required to retain half of the original film[17] are collected in Table 1. Contrast is calculated from the gel dose and the insolubilization dose and is 0.76 for **2a** and 0.81 for **2c**.

In order to obtain images of higher aspect ratio, a thicker film (1.5 μm thick) of **2a** was obtained and irradiated through a mask with features of different size (1–100 μm slits). The minimum image resolvable under present conditions was that of the 2 μm bars, as shown in the scanning electron microscopy (SEM) micrograph of the image, Figure 6.

Structure–Reactivity Relationship. As is apparent in Table 1, the reactivities of the polymers as

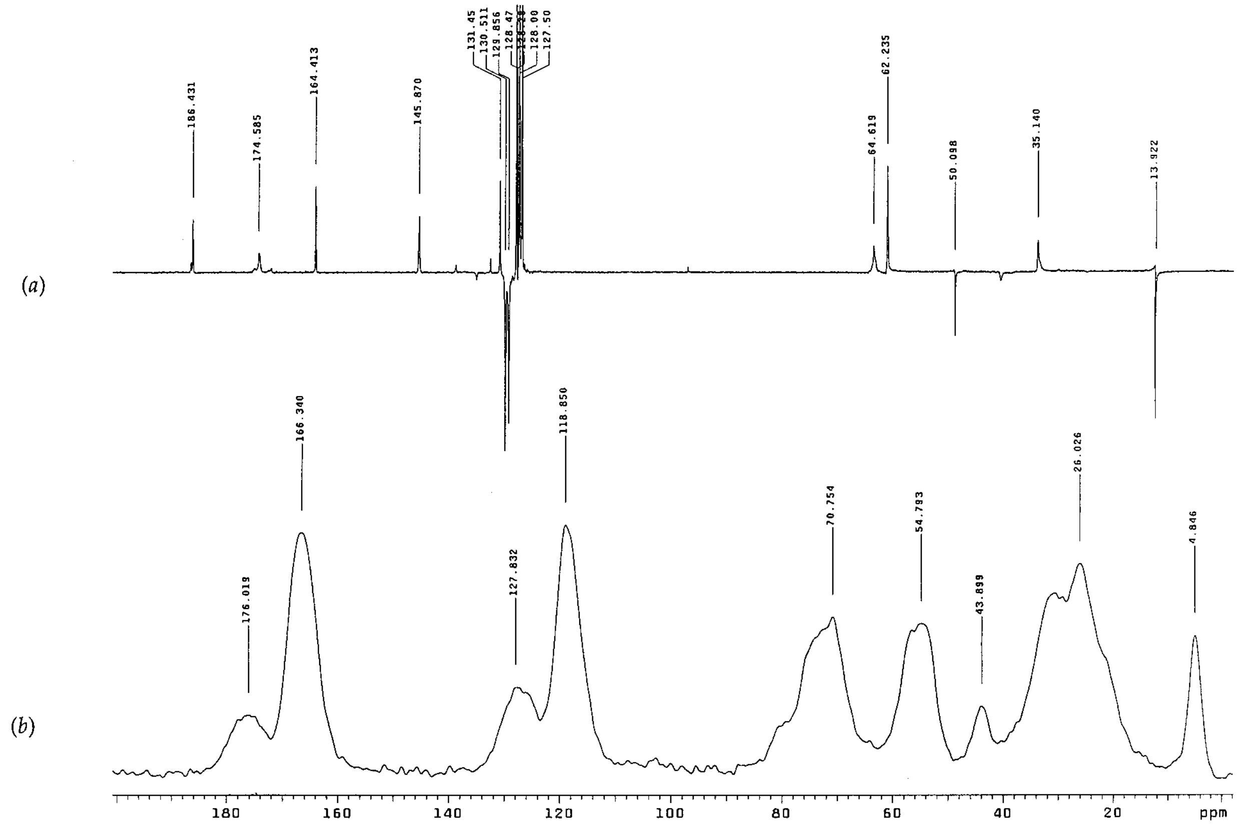


Figure 2. ^{13}C NMR spectra of **2b** before (a, APT, in C6D6) and after irradiation (b, cross-polarization magic angle spinning (CPMAS).

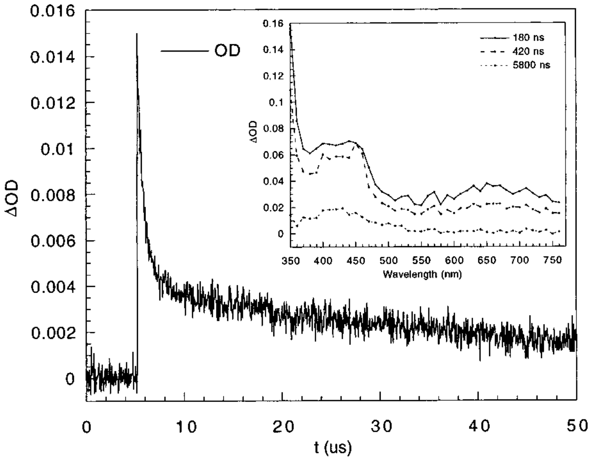


Figure 3. Transient decay trace detected at 440 nm from a benzene solution (2.0 mg/mL) of **2a**. Inserted are transient absorption spectra at different delay times.

indicated by the lifetimes of the ketyl radicals and the sensitivities measured in imagewise irradiations are related closely to their structures. Because the phenylglyoxylate chromophores are bonded by a polymeric backbone, interchromophore reactions dominate over the Norrish type II photolysis that would be expected in a monomeric counterpart. The lifetimes of the resulting ketyl radicals are significantly shorter than are those of a monomeric radical in solution. Furthermore, the reactivity of the ketyl radical depends on the extent of the restriction imposed by the polymer backbone. As the distance between the backbone and the ketyl radical center shortens, movement of the radicals become further confined so that coupling of the radicals is facilitated. This leads to a shortening of radical lifetime as well as improvement in the film sensitivity. From the data in Table 1, one can conclude that polymer **3** is more reactive than **2**. This is likely due to the bulky aromatic ring between the backbone and the ketyl radical center of **2** preventing the approach of the pendant radicals.

Conclusions

The polymeric alkyl phenylglyoxylate chromophore reacts differently from its monomeric counterpart in that hydrogen abstraction occurs exclusively between pendant chromophores. The resulting radicals couple resulting in cross-linking of the polymer. Thin films made from this polymer are sensitive to imagewise irradiation. The reactivities of the polymers are closely related to their structural features.

Experimental Section

Materials. Benzene was distilled from sodium benzophenone ketyl under an argon atmosphere immediately before use. Other chemicals were the highest grade obtainable from commercial sources and used as received. Silica gel 60 Å (60–200 mesh) used in column chromatography was obtained from J. T. Baker Chemical Co. NMR spectra were taken with a Varian Gemini 200 NMR or an Unity Plus 400 NMR spectrometer and chemical shifts are in ppm with TMS as the internal standard. GC/MS measurements were taken on a Hewlett-Packard 5988 mass spectrometer coupled to an HP 5880A GC with a 30 m × 0.25 mm i.d. × 0.25 μm film thickness DB-5 ms column (J & B Scientific). Gel permeation chromatography was performed with an HP 1050 series high-performance liquid chromatograph equipped with an HP 1047A refractive index detector and a PLgel 5 μm mixed-C 300 × 7.5 μm column. HPLC grade THF was used as eluent. Polyacrylate standard samples were obtained from Scientific Polymer Products, Inc. Infrared spectra were taken with a

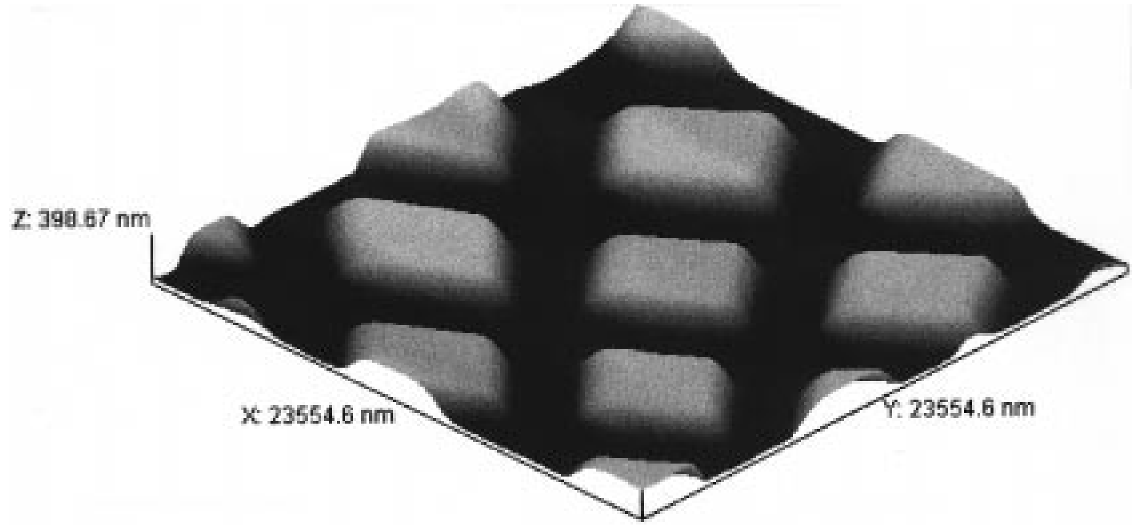


Figure 4. AFM micrograph of the image produced by **2a** at the insolubilzation dose.

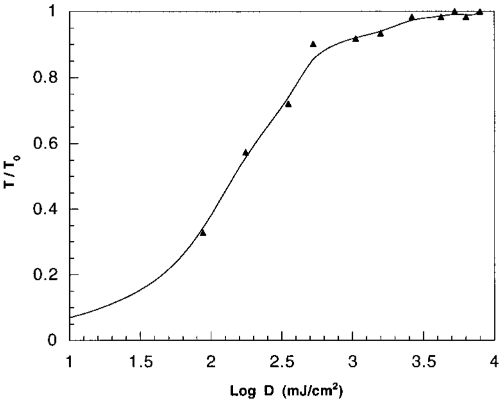
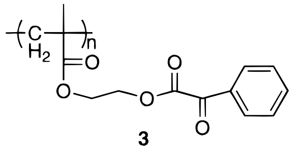


Figure 5. Sensitivity curve for **2a** when subjected to image-wise irradiation.

Table 1. Transient Lifetimes and Film Sensitivities

	distance[a] (no. of atoms)	τ_{triplet} (μs)	$\tau_{\text{ketyl radical}}$ (μs)	sensitivity (mJ/cm^2)
2a	8	1.2	47	200
2c	7	0.94	28	173
3	6	1.0	1.8	110

[a] Distance between the ketyl radical center and the polymer backbone.



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Galaxy series 6020 FTIR spectrometer. Transmission electron microscopy (TEM) grids were purchased from Electron Microscopy Sciences. SEM micrographs were obtained on a Hitachi S-2700 scanning electron microscope. AFM micrographs were obtained using a Metris-2000 Atomic Force Microscope manufactured by Burleigh Instruments, Inc. Silicon tips with a spring constant of $K = 0.1$ N/m were used. A 25 × 25 μm scan module was used with the reference force set at 5.0 V. Elemental analyses were carried out by Atlantic Microlab, Inc.

Polymer films (about 200 nm in thickness) were prepared by spin coating from a 10% (w/w) benzene solution of **2** at 6000 rpm for 20 s with a Headway Research, Inc., spin-coater onto silicon wafers (Si-Tech, Inc.) of appropriate sizes. Thicker films (1.5 μm) were prepared from a 50% (w/w) benzene solution of **2**. Film irradiations were performed on a setup using a high-pressure mercury arc lamp (200 W) as the irradiation source. Defocused UV irradiation was filtered through a 365 nm filter (bandwidth ~40 nm). The distance from the film to the lamp remained fixed at 11 cm. Photon flux from the irradiation source was measured by a Scientech 365 power and energy meter with its photomultiplier tube positioned in the same place as the target films. Irradiation in solution was carried out in a Rayonet RPR-100 photoreactor equipped with 16 350 nm GE F8T5.BLB UV lamps.

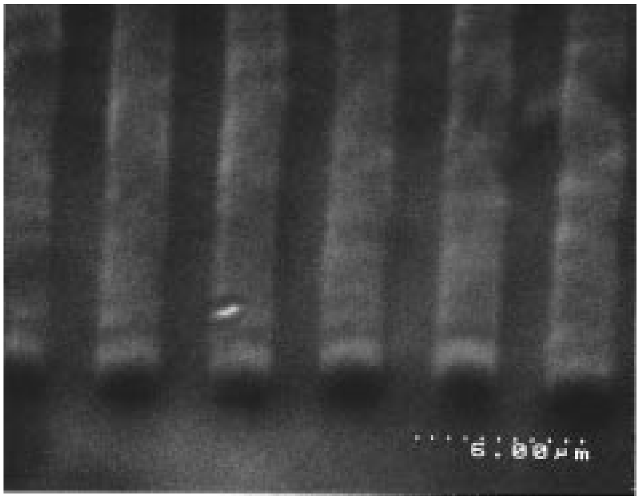

Figure 6. SEM micrograph of the image produced by **2a**.

Time-Resolved Laser Flash Photolysis. Nanosecond laser flash photolyses were carried out on a setup described by Ford and Rodgers[18] using a Q-switched Nd:YAG laser as a pump light. Argon was passed through the sample cuvette for 10 min before and during the experiments.

Ethyl *p*-2′-Methacryloylethylphenylglyoxylate (1a). Ethyl oxalyl chloride (6.0 g, 44 mmol), aluminum chloride (7 g, 52 mmol), and 30 mL of anhydrous methylene chloride were placed in a 100 mL flask equipped with a magnetic stirrer and suspended in an ice−salt bath. After the mixture was stirred for 5 min, crude phenethyl methacrylate (4.7 g, 25 mmol, prepared from phenethyl alcohol and methacryoyl chloride) in 20 mL of dry methylene chloride was added dropwise over a period of 30 min. The mixture was allowed to warm to room temperature and stirred for 3 more h. The mixture was then poured over 150 g of crushed ice and 80 mL of concentrated hydrochloric acid. The mixture was washed with 0.1 N sodium hydroxide, 0.1 N sodium bicarbonate, and water each three times. The organic layer was collected and dried over $MgSO_4$. Pure (4.0 g, 14 mmol, 56% yield) **1a** was obtained after column chromatography using hexanes (H)/ethyl acetate (EA) = 8/1 as eluents (R_f in H/EA = 5/1 is 0.34): ^{1}H NMR (200 MHz,

$CDCl_3$) δ 1.42 (t, $J = 7.0$ Hz, 3H), 1.90−1.91 (m, 3H), 3.08 (t, $J = 6.6$ Hz, 2H), 4.39 (t, $J = 6.6$ Hz, 2H), 4.45 (q, $J = 7.0$ Hz, 2H), 5.54−5.56 (m, 1H), 6.06−6.07 (m, 1H), 7.39 (d, $J = 8.0$ Hz, 2H), 7.95−7.99 (m, 2H); ^{13}C NMR (APT, 50 MHz, $CDCl_3$) δ 13.98, 18.11, 35.15, 62.17, 64.14, 125.62, 129.30, 130.17, 130.86, 135.94, 145.88, 163.71, 166.99, 185.82; MS (EI, 70 ev) 69 (9.7), 103 (16), 131 (100), 204 (7.5), 217 (32, $M^+ - 73$).

Ethyl *p*-2′-Acryloylethylphenylglyoxylate (1b). Similar procedures to those outlined for **1a** produced **1b** in 61% yield (R_f in H/EA = 5/1 is 0.27): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42 (t, $J = 7.2$ Hz, 3H), 3.07 (t, $J = 6.8$ Hz, 2H), 4.41 (t, $J = 6.8$ Hz, 2H), 4.45 (q, $J = 7.2$ Hz, 2H), 5.83 (dd, $J_1 = 10.4$ Hz , $J_2 = 1.2$ Hz, 1H), 6.09 (dd, $J_1 = 17.2$ Hz , $J_2 = 10.4$ Hz, 1H), 6.38 (dd, $J_1 = 17.2$ Hz , $J_2 = 1.6$ Hz, 1H), 7.37−7.40 (m, 2H), 7.96−7.98 (m, 2H); ^{13}C NMR (APT, 50 MHz, $CDCl_3$) δ 14.06, 35.17, 62.28, 64.01, 128.08, 129.43, 130.28, 130.97, 131.06, 145.73, 163.75, 165.88, 185.86; MS (EI, 70 ev) 55 (17), 77 (9.6), 90 (8.0), 103 (17), 131 (100), 203 (56, $M^+ - 73$).

Poly(ethyl *p*-2′-Methacryloylethylphenylglyoxylate) (2a). **1a** (2.0 g) and 0.06 g of AIBN were dissolved in 30 mL of dry benzene. The solution was stirred for 15 min under a stream of dry nitrogen and then refluxed for 3 h. The resulting solution was concentrated to 10 mL and poured into 250 mL of methanol. The resulting precipitate was collected. **2a** (1.15 g) was obtained by further precipitating the product twice from methanol. Anal. Calcd: C, 66.19; H, 6.24. Found: C, 66.29; H: 6.29. The molecular weight was measured by GPC: $M_w = 22\,911$, $M_n = 9823$. Differential scanning calorimetry (DSC) measurements showed no T_g between 50 and 180 °C: ^{1}H NMR (200 MHz, C_6D_6) δ 1.04 (m, 6H), 2.06 (br, 2H), 2.80 (br, 2H), 4.12 (m, 4H), 7.17 (m, 2H), 8.06 (m, 2H); ^{13}C NMR (APT, 50 MHz, C_6D_6) δ 13.96, 14.12, 34.85, 45.20, 45.40, 62.09, 65.04, 129.91, 130.48, 131.59, 146.16, 164.39, 177.19, 186.34.

Poly(ethyl *p*-2′-acryloylethylphenylglyoxylate) (2b). Similar procedures to those described for **2a** produced **2b** in 60% yield. Anal. Calcd: C, 65.20; H, 5.83. Found: C, 65.33; H, 5.85. The molecular weight was measured by GPC: $M_w = 27\,871$, $M_n = 9254$. DSC measurements showed no T_g between 50 and 180 °C. ^{1}H NMR (200 MHz, C_6D_6) δ 1.06 (t, $J = 7.0$ Hz, 3H), 2.45 (br, 2H), 2.68 (br, 2H), 2.86 (br, 2H), 4.15 (m, 4H), 7.19 (m, 2H), 8.03 (m, 2H); ^{13}C NMR (APT, 50 MHz, C_6D_6) δ 13.90, 35.12, 50.10, 62.24, 64.60, 129.86, 130.51, 133.17, 145.87, 164.41, 174.59, 186.43.

Poly(ethyl *p*-acryloylmethylphenylglyoxylate) (2c) was isolated in 72% yield from the attempted reaction to synthesize **1c** (same procedure as described for **1a**): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.37 (t, $J = 7.0$ Hz, 3H), 2.72 (br, 3H), 3.79 (s, 2H), 4.40 (m, 2H), 6.98 (m, 2H), 7.84 (m, 2H); ^{13}C NMR (APT, 50 MHz, $CDCl_3$) δ 13.98, 38.68, 41.44, 50.52, 62.24, 128.90, 130.39, 148.84, 163.73, 172.23, 185.75.

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References and Notes

(1) Contribution No. 335 from the Center for Photochemical Sciences.

(2) Schönberg, A.; Latif, N.; Moubasher, R.; Sina, A. *J. Chem. Soc.* **1951**, 1364−1368.

(3) Huyser, E. S.; Neckers, D. C. *J. Org. Chem.* **1964**, *29*, 276−278.

(4) (a)Schönberg, A.; Mustafa, A. *Chem. Rev.* **1947**, *40*, 181. (b) Moore, W. M.; Hammond, G. S.; Foss, R. P. *J. Am. Chem. Soc.* **1961**, *83*, 2789−2794. (c) Pitts, J. N., Jr.; Letsinger, R. L.; Taylor, R. P.; Patterson, J. M.; Rectenwald, G.; Martin, R. B. *J. Am. Chem. Soc.* **1959**, *81*, 1068−1077.

(5) Hu, S.; Neckers, D. C. *J. Org. Chem.* **1996**, *61*, 6407−6415 and references therein.

(6) (a) Fodor, S. P. A.; Read, J. L.; Pirrung, M. C.; Stryer, L.; Lu, A. T.; Solas, D. *Science* **1991**, *251*, 767−773. (b)Wallraff, G.; Labadie, L.; Brock, P.; DiPietro, R.; Nguyen, T.; Huynh, T.; Hinsberg, W.; McGall, G. *CHEMTECH* **1997**, *29* (2), 22−32.

(7) Reiser, A. *Photoreactive Polymers - The Science and Technology of Resist*; Wiley: New York,1989.

(8) Nagamatsu, G.; Inui, H. *Photosensitive Polymers*; Kodansha: Tokyo, 1977.

(9) (a) Reddy, A. V. R.; Subramanian, K.; Krishnasamy, V.; Ravichandran, J. *Eur. Polym. J.* **1996**, *32*, 919−926. (b) Nishikubo, T.; Iizawa, T.; Tsuchiya, K.*; Makromol. Chem., Rapid Commun.* **1982**, *3*, 377−383. (c) Shirai, M.; Kuwahara, M.; Tanaka, M. *J. Polym. Sci., Polym. Chem.* **1990**, *28*, 2563−2567. (d) Watanabe, S.; Harashima, S.; Tsukada, N. *J. Polym. Sci., Polym. Chem.* **1986**, *24*, 1227−1237. (e) Ichimura, K.; Nishio, Y. *J. Polym. Sci., Polym. Chem.* **1987**, *25*, 1579−1590. (f) Nishikubo, T.; Iizawa, T.; Takahashi, E.; Nono, F. *Macromolecules* **1985**, *18*, 2131−2135. (g) Chen, Y.; Hong, R. T. *J. Polym. Sci., Polym. Chem.* **1997**, *35*, 2999−3008. (h) Kannam, P.; Kishore, G. *Polymer* **1997**, *38*, 4349−4355. (i) Achari, A. E.; Coqueret, X. *J. Polym. Sci., Polym. Chem.* **1997**, *35*, 2513−2520. (j) Marugavel, S. C.; Kaliyappan, T. Swaminathan, C. S.; Kannan, P. *J. Appl. Polym. Sci.* **1997**, *65*, 2151−2157. (k) Konno, K.; Veda, M.; Cassidy, P.; Fitch, J. W. *J. Macromol. Sci.—Pure Appl. Chem.* **1997**, *A34*, 929−939. (l) Lukác, I.; Kósa, Cs.; Salz, U.; Moszner, N. *J. Photochem. Photobiol., A: Chem.* **1997**, *102*, 259−263. (m) Murugavel, S. C.; Swaminathan, C. S.; Kannan, P. *Polymer* **1997**, *38*, 5179−5183.

(10) Hu, S.; Neckers, D. C. *J. Mater. Chem.* **1997**, *7*, 1737−1740.

(11) Hu, S.; Neckers, D. C. *J. Org. Chem.* **1997**, *62*, 755−757.

(12) Jager, W. F.; Lungu, A.; Chen, D. Y.; Neckers, D. C. *Macromolecules* **1997**, *30*, 780−791.

(13) Hu, S., Meijiritski, A. M.; Neckers, D. C. *Chem. Mater.* **1997**, *9*, 3171−3175.

(14) Initial studies were performed using benzene. Other solvents, e.g., toluene, were also shown to work as well. Data reported herein were obtained by using benzene as the developing solvent.

(15) Obtained by spin coating the polymer solution on a round silicon wafer (75 mm in diameter) and cutting it into smaller pieces (13 × 13 mm).

(16) 5 μm bars separating 7.5 × 7.5 μm rectangular holes.

(17) Thompson, L. F.; Willson, C. G.; Bowden, M. J. *Introduction to Microlithography*, 2nd ed.; ACS Professional Reference Book; American Chemical Society: Washington, DC, 1994.

(18) Ford, W. E.; Rodgers, M. A. J. *J. Phys. Chem.* **1994**, *98*, 3822−3831.

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