Chem. Mater. **1997,** *9,* 3171−3175

Photoreactions of Polymeric (Meth)acryloylethyl Phenylglyoxylate—Reactivity in Solution and Film[1]

Shengkui Hu, Alexander Mejiritski, and D. C. Neckers*

Center for Photochemical Sciences, Bowling Green State University,
Bowling Green, Ohio 43403

Received July 7, 1997[⊗]

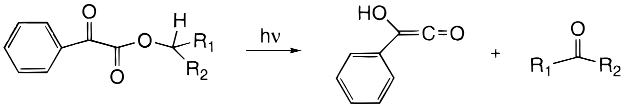
Photochemical reactions of poly[(meth)acryloylethyl phenylglyoxylate] in aprotic solvents were studied, and cross-linking of the polymer caused by a hydrogen abstraction reaction between pendent phenylglyoxylate chromophores was observed. The Norrish type II reaction, a primary photochemical process of the phenylglyoxylate chromophore, does not compete with this hydrogen abstraction. Poly[(meth)acryloylethyl phenylglyoxylate] was tested as a negative-tone photoimaging material and found to have a sensitivity of 110 mJ·cm^{-2} and a contrast ratio of 0.75 after imagewise irradiation. The resolution achieved under conventional laboratory conditions was 2 μm.

Introduction

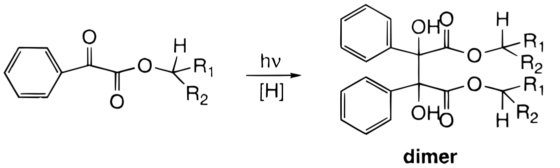
Photochemical reactions of alkyl phenylglyoxylates have been studied extensively. It has been shown that in aprotic solvents, Norrish type II photolysis (Scheme 1) is the predominant process. Intermolecular hydrogen-abstraction-induced radical chain reactions, producing, among other products, dialkyl 2,3-dihydroxy-2,3-diphenylsuccinate (dimer in Scheme 2), become competitive when the initial concentration of the phenylglyoxylate increases.[2] In protic solvents, the phenylglyoxylate chromophore can be photoreduced efficiently to furnish dimer as the major product (Scheme 2).[3,4]

In a systematic study of the photochemical reactions of alkyl phenylglyoxylates bearing different functionalities in the alkyl moiety,[5] we found that (meth)acryloylethyl phenylglyoxylate reacts uniquely by self-polymerizing upon irradiation.[6] Because of our interest in studying photochemical reactions on polymeric surfaces, we studied poly[(meth)acryloylethyl phenylglyoxylate] synthesized by 2,2′-azobisisobutyronitrile (AIBN)-initiated polymerization as a potential substrate for carrying out organic reactions on a thin film. We observed that the polymer is light sensitive and exhibits different solubility for the irradiated and nonirradiated portions in certain solvents.

Scheme 1



Scheme 2



Polymer insolubilization has long been recognized as being achieved by photo-cross-linking, and the great majority of negative resists developed prior to this have been based on the formation of cross-links.[7] Though such imaging methodology has long since been surpassed in most industrial applications, photochemical reactions on surfaces remain an important area of research investigation, particularly with the developments in combinatorial synthesis.[8]

In the present paper, we report the synthesis and photochemistry of poly[(meth)acryloylethyl phenylglyoxylate]. It appears to have interesting and useful properties as a photoreactive film.

Results and Discussion

Solution Photochemistry. (Meth)acryloylethyl -phenylglyoxylates (**1**) were synthesized in good yields by *N*,*N*-dicyclohexylcarbodiimide (DCC) esterification of benzoylformic acid. Polymerization was initiated by AIBN in refluxing benzene in which **Poly-1** dissolves well. Upon irradiation (350 nm) of a **Poly-1** solution in benzene (0.05 M), a white precipitate appears. Products expected from Norrish type II photolysis, e. g., benzaldehyde, were not detected by GC investigations of the reaction mixture (Scheme 3).

The absence of Norrish type II products in **Poly-1** was initially surprising since alkyl phenylglyoxylates possessing γ-hydrogens undergo primarily the Norrish type II reaction in dilute (~0.01 M) benzene solutions.

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1997.

(1) Contribution No. 320 from the Center for Photochemical Sciences.

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

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

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

(5) (a) Hu, S.; Neckers, D. C. *J. Org. Chem.* **1997**, *62*, 564. (b) Hu, S.; Neckers, D. C. *J. Org. Chem.* **1997**, *62*, 755. (c) Hu, S.; Neckers, D. C. *Tetrahedron* **1997**, *53*, 2751. (d) Hu, S.; Neckers, D. C. *Tetrahedron* **1997**, *53*, 12771. (e) Hu, S.; Neckers, D. C. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1751.

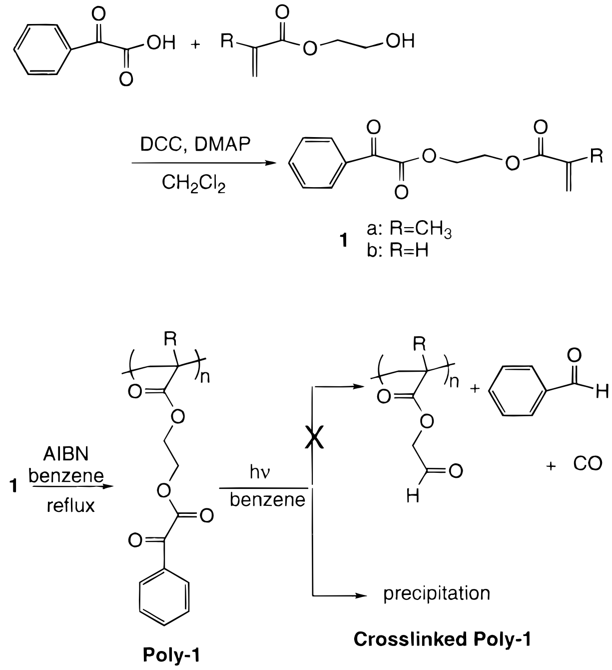
(6) Hu, S.; Neckers, D. C. *J. Org. Chem.* **1997**, *62*, 6820.

(7) Reiser, A.; Shih, H−Y.; Yeh, T−F.; Huang, J−P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2428.

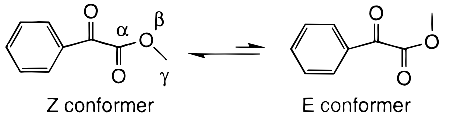
(8) For leading reviews: (a) Thompson, L. A.; Ellman, J. A. *Chem. Rev. (Washington, D.C.)* **1996**, *96*, 555. (b) Früchtel, J. S.; Jung, G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 17. (c) Nefzi, A.; Ostresh, J. M.; Houghten, R. A. *Chem. Rev. (Washington, D.C.)* **1997**, *97*, 449.

S0897-4756(97)00591-7 CCC: $14.00

Scheme 3

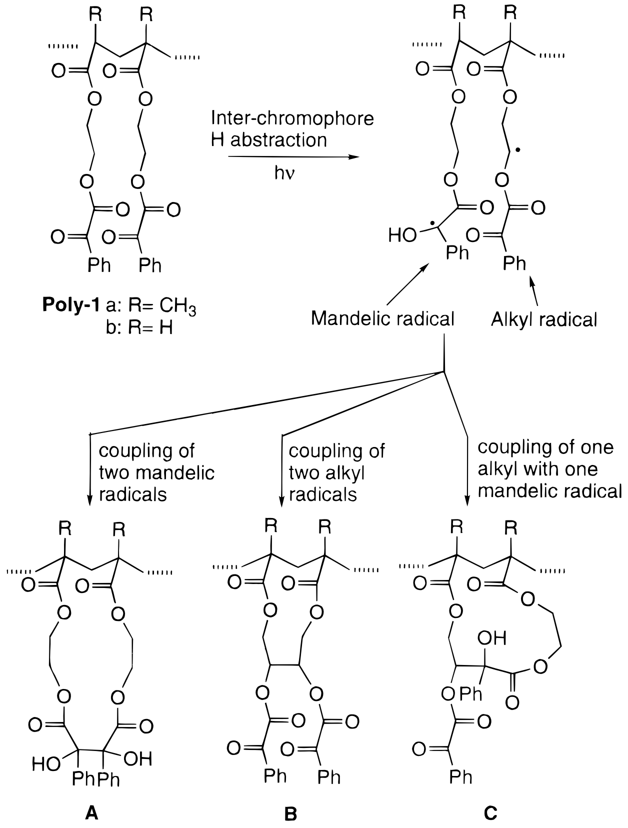


Scheme 4



Photochemical processes induced by intermolecular hydrogen abstraction become competitive only when concentration of the starting esters is higher (~0.1 M).[2] Because of the absence of the expected Norrish type II products from the pendent phenylglyoxylates, chemical changes in the benzene solution of **Poly-1** have to be attributed to analogous "intermolecular" processes between the pendent chromophores (referred to as "interchromophore processes" hereafter). Domination by interchromophore reactions when **Poly-1** is irradiated in benzene can be imagined if one considers the potential proximity of phenylglyoxylate moieties enforced by the polymeric chain. Even though the polymer concentration in solution is not high, the phenylglyoxylate chromophores are close since their movement is restricted by the acrylic backbone, *i.e.*, the local concentration of the chromophore is high. On the other hand, the Norrish type II reaction of phenylglyoxylates is known to be slow ($k = 6.5 \times 10^5\ \mathrm{s}^{-1}$)[2] because of the unfavorable conformation for γ-hydrogen abstraction adopted by these α-keto esters.[5a,e] In the most stable *Z* conformer of an ester, its γ-hydrogens are beyond the distance from the ketone carbonyl oxygen (ca. 2.8 Å)[9] required for reaction (Scheme 4). The inherently slow rate of the Norrish type II γ-hydrogen abstraction in phenylglyoxylates makes this impossible to compete with the intramolecular interchromophore processes in **Poly-1**.

Scheme 5



Three probable substructures of **Crosslinked Poly-1** a: R= CH_3
b: R= H

Cross-Linking Mechanism. The precipitates resulting from the irradiation of benzene solutions of **Poly-1** possess the same elemental composition as the original polymers, and no small molecules expected from the Norrish type II photolysis have been detected. A mechanism involving an interchromophore hydrogen abstraction between pendent phenylglyoxylates, which induces cross-linking of the polymer, is proposed to account for these experimental observations (Scheme 5).

Interchromophore hydrogen abstraction from phenylglyoxylate triplet produces two kinds of radicals, the mandelic and alkyl radicals. Both are expected to be relatively stable because their radical centers are stabilized by electron-donating substituents. (The methyl mandelate radical was observed to have a lifetime of 80 μs in a benzene solution.)[2] Reactions between radicals of these kinds would result in three different substructures in the cross-linked polymer. Coupling of two mandelic radicals results in succinate substructure **A**. Coupling of two alkyl radicals produces **B** and radical cross-coupling furnishes **C**. The photoactive carbonyl groups susceptible to cross-linking remain in substructures **B** and **C**. These residual functional groups can be further activated by light and react similarly to produce "secondary" cross-links.

Laser Flash Photolysis. Transient absorptions (insert in Figure 1) were detected when a benzene solution of **Poly-1a** was flashed with a 355 nm laser pulse. The trace monitored at 420 nm decays biexponentially with the lifetime of the first component being 1.0 μs and that of the second component being 1.8 μs. We have demonstrated that both the triplet excited state of an alkyl phenylglyoxylate and the mandelic radical derived thereafter absorb from 420 to 440 nm.[2] The decay trace in Figure 1 represents the deactivations of

---

[9] (a) Wagner, P. J.; Meador, M. A.; Zhou, B.; Park, B.-S. *J. Am. Chem. Soc.* **1991**, *113*, 9630. (b) Wagner, P. J.; Zhou, B.; Hasegawa, T.; Ward, D. L. *J. Am. Chem. Soc.* **1991**, *113*, 9640. (c) Gudmundsdottir, A. D.; Lewis, T. J.; Randall, L. H.; Scheffer, J. R.; Rettig, S. J.; Trotter, J.; Wu, C.-H. *J. Am. Chem. Soc.* **1996**, *118*, 6167.

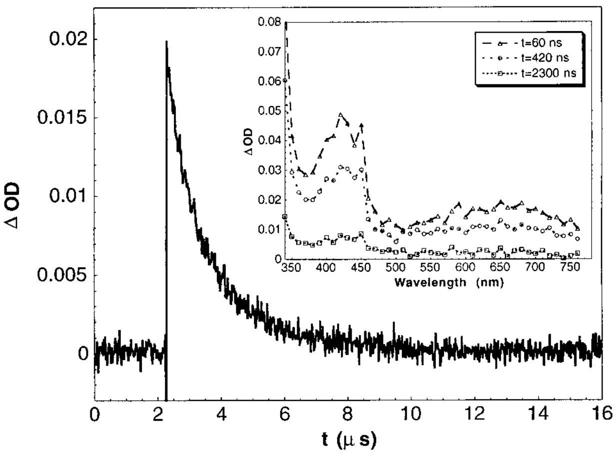


Figure 1. Decay trace monitored at 420 nm when **Poly-1a** was flashed in benzene (0.05 M). Insert is the transient absorption spectra at different delay times after a laser flash.

both. The first component is attributed to the phenylglyoxylate triplet, and the second to the mandelic radical.

It is noted that the triplet lifetime of **Poly-1a** is not significantly altered compared to that of monomeric alkyl phenylglyoxylates.[2] This is surprising considering the fact that most nonconjugated diketones undergo internal self-quenching, i.e., the ground state chromophore quenches the excited moiety in the same molecule, and this significantly shortens the triplet lifetimes of diketones compared to the corresponding monoketones.[10] However, there are several studies on poly(phenyl vinyl ketones) suggesting that such internal quenching does not occur in the triplet state of these molecules because triplet energy transfer between equivalent chromophores is very efficient.[11] Therefore, we believe that internal quenching between phenylglyoxylate chromophores does not occur in poly[(meth)-acryloylethyl phenylglyoxylate].

On the other hand, the lifetime of the mandelic radical attached to the polymer chain in **Poly-1a** is significantly shorter than that of the methyl mandelic radical (80 μs) in a benzene solution. This is partly the result of the fact that the coupling of mandelic radicals in **Poly-1a** is a facile intramolecular process and the radical is readily deactivated. The coupling of two mandelic radicals after photolysis of monomeric alkyl phenylglyoxylates in benzene is an intermolecular process.

Solid Film Photochemistry. Having observed cross-linking when **Poly-1** was irradiated in a benzene solution, we postulated that a similar process would take place in solid polymer film. Imagewise irradiation of a spin-coated film of **Poly-1a** on the surface of a silicon wafer was carried out using 365 nm light.[12] After brief subsequent immersion in benzene, the irradiated areas of the film were insoluble and remained on the silicon wafer, while the nonirradiated portions of the film were completely removed from the substrate surface. This differential solubility became the basis for the negative-tone imaging system.

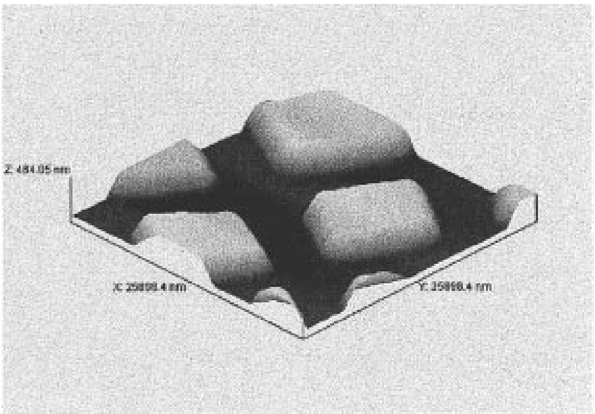


Figure 2. AFM micrograph of an image produced when the irradiation dose is equal to D_i.

A number of films of uniform thickness (~200 nm) were obtained by spin-coating a **Poly-1a** solution onto a silicon wafer (76 mm in diameter) and then cutting the wafer into small square pieces (~13 × 13 mm).[13] These samples were subjected to different doses of imagewise UV irradiation filtered through a 365 nm filter (bandwidth ~ 40 nm). Transmission electron microscopy grids T2000-Cu (EMS) with holes of 7.5 × 7.5 μm and bars of 5 μm separating the holes were used to simulate soft contact masks. After exposure, the samples were developed by immersing them in a dry benzene solution[14] for 30 s. The thickness of the cross-linked film in the exposed areas (7.5 × 7.5 μm square mounds) was evaluated by atomic force microscopy (AFM), and a sensitivity curve was constructed by plotting the normalized thickness of the remaining film versus the accumulated exposure dose. The minimum dose required to observe the insolubilized residue, the gel dose, D_g, is 30 mJ/cm^2. The minimum dose necessary to produce the insolubilized film of maximum thickness (which in this case is equal to the thickness of the initial film), the insolubilization dose, D_i, is 663 mJ·cm^{-2}. The sensitivity of the negative image, D_s, if defined as the dose required to insolubilize 50% of the initial film, is 110 mJ·cm^{-2} for **Poly-1a**. The contrast, γ, is calculated to be 0.75.[15]

An AFM micrograph of the image produced by an irradiation dose equal to D_i is shown in Figure 2. The nonirradiated portion of the film was dissolved down to the substrate.

To test the resolution attainable by this system and its ability to produce three-dimensional relief images of at least 1:1 aspect ratio, a thicker film (1.5 μm) on a 20 × 20 mm silicon substrate was exposed through a soft contact resolution mask containing line patterns of

---

(10) Wagner, P. J.; Frerking, H. W., Jr. *Can. J. Chem.* **1995**, *73*, 2047.

(11) (a) David, C.; Demarteau, W.; Geuskens, G. *Polymer* **1967**, *8*, 497. (b) Golemba, F. J.; Guillet, J. E. *Macromolecules* **1972**, *5*, 212. (c) Somersall, A. C.; Dan, E.; Guillet, J. E. *Macromolecules* **1974**, *7*, 233. (d) Encinas, M. V.; Funabashi, K.; Scaiano, J. C. *Macromolecules* **1979**, *12*, 1167. (e) Das, P. K.; Encinas, M. V.; Scaiano, J. C. *J. Photochem.* **1980**, *12*, 357. (f) Scaiano, J. C.; Selwyn, J. C. *Macromolecules* **1981**, *14*, 1723.

(12) (12) **Poly-1b** performs essentially the same as **Poly-1a** with regard to the photolithographic tests. **Poly-1a** was chosen to obtain more quantitative information.

(13) Reichmanis, E.; Galvin, M. E.; Ulrich, K. E.; Mirau, P.; Heffner, S. A. *Polymeric Materials for Microelectronic Applications: Science and Technology*; ACS Symp. Ser. 579; American Chemical Society: Washington, DC, 1994; p 52.

(14) Preliminary experiments were carried out in benzene to be consistent with the conditions for solution chemistry study. To avoid the health hazards of benzene, dry toluene was tested as the developing solvent and proven to work as well as benzene.

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

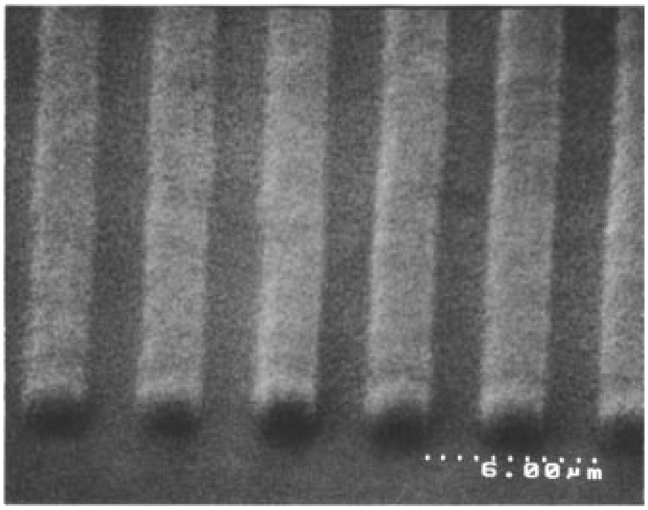


Figure 3. SEM micrograph of the resolved 2 μm line patterns.

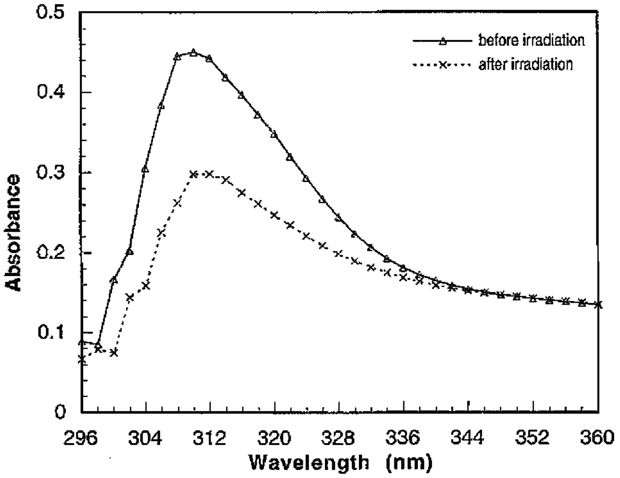


Figure 4. The UV absorbance of a resist film before and after irradiation.

various widths. The accumulated exposure dose used was equal to that of D_i. The smallest line clearly resolved at this exposure dose is 2 μm wide (Figure 3).[16]

To estimate the degree of cross-linking necessary to insolubilize the film, the UV absorption spectra of a 200 nm thick **Poly-1a** film on a Pyrex substrate was recorded before and after irradiation with a dose equal to that of D_i. After exposure, the absorbance (optical density) at 320 nm, which is attributed to the original phenylglyoxylate chromophore, decreased to half of its original intensity (Figure 4). This suggests that approximately half of the phenylglyoxylate chromophores are consumed when insolubilization is achieved.

After a **Poly-1a** film was exposed through a T2000-Cu mask as described above and examined by AFM prior to the development step, little topological contrast (~3 nm) between exposed and nonexposed portions of the film was observed. The contrast between the two portions became quite distinct when a lateral force image was collected in parallel with the topographical one (Figure 5). Photochemically induced cross-linking apparently results in a significant change in the friction on the surface of the exposed portions of the film. The AFM cantilever experiences very different torques as it is scanned across the surfaces of exposed and nonexposed areas.

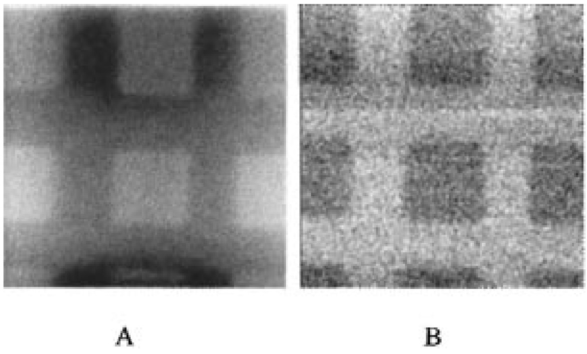


Figure 5. AFM micrographs of an imagewise irradiated polymer film prior to development: (A) the topological image and (B) the lateral force image.

Conclusions

In aprotic solvent, polymeric (meth)acryloylethyl phenylglyoxylate undergoes intramolecular hydrogen abstraction between pendent chromophores upon irradiation. No Norrish type II process within a single phenylglyoxylate chromophore is observed. The characteristic requirements for poly[(meth)acryloylethyl phenylglyoxylate] to be used as a photoresist have been examined. Its resolution, sensitivity, and contrast measured in a conventional laboratory environment indicate that poly[(meth)acryloylethyl phenylglyoxylate] is a promising photoreactive material.

Experimental Section

Material. Benzene (Aldrich) was distilled over sodium benzophenone ketyl under argon. Other chemicals were obtained from commercial sources and used as received. NMR spectra were taken with a Varian Gemini 200 NMR spectrometer in $CDCl_3$, 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). UV absorption spectra were recorded on an HP 8452A diode-array UV/visible spectrophotometer. Gel permeation chromatography was performed with an HP 1050 series HPLC 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. Silica gel (60 Å, 60−200 mesh) used in column chromatography was obtained from J. T. Baker Chemical Co. TEM grids were purchased from Electron Microscopy Sciences. Elemental analysis was carried out by Atlantic Microlab, Inc. High-resolution mass spectra were obtained from the University of Illinois at Urbana−Champaign.

Polymer films (about 200 nm in thickness) were prepared by spin-coating from a 10% (w/w) benzene solution of **Poly-1a** 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 **Poly-1a**. Film irradiations were performed on a custom-made 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

---

(16) The experiment was performed in a conventional laboratory environment, *i.e.*, not dust-free conditions.

F8T5.BLB UV lamps. 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.

Time-Resolved Laser Flash Photolysis. Nanosecond laser flash photolysis was carried out on a setup described previously[17] using the third harmonic of a Q-switched Nd:YAG laser as the excitation source. The sample solution in a quartz curette was purged with argon for 5 min before and during the experiment. The samples were excited with 355 nm pulses (pulse width ca. 7 ns).

Methacryloylethyl Phenylglyoxylate (1a). To a stirred anhydrous dichloromethane solution of 1.5 g (10 mmol) of benzoylformic acid, 1.45 g (11 mmol) of 2-hydroxyethyl methacrylate, and 122 mg (1.0 mmol) of 4-(dimethylamino)pyridine on an ice bath was added an anhydrous dichloromethane solution of 2.3 g (11 mmol) of DCC dropwise. The mixture was stirred on an ice bath for 10 min, allowed to warm to room temperature, and then stirred for another 8 h. The urea which precipitated was filtered and the resulting solution washed three times each with water, 0.5 N HCl, and a saturated sodium bicarbonate solution. The solution was then dried over anhydrous $MgSO_4$ and concentrated. The title compound (2.3 g; 90%) was obtained after column chromatography (hexanes: ethyl acetate = 15:1), ^{1}H NMR (200 MHz) δ 1.95 (t, $J = 1.3$ Hz, 3H), 4.47−4.52 (m, 2H), 4.64−4.69 (m, 2H), 5.61−5.63 (m, 1H), 6.15−6.17 (m, 1H), 7.47−7.55 (m, 2H), 7.64−7.68 (m, 1H), 7.99−8.04 (m, 2H). ^{13}C NMR (50 MHz) δ 18.22, 61.93, 63.53, 126.37, 128.90, 130.01, 132.27, 135.03, 135.69, 163.46, 166.93, 185.80. MS 41 (6.9), 77 (21.7), 105 (100), 113 (5.4), 174 (0.1), 200 (0.1). HRMS m/z calculated for $C_{14}H_{14}O_5$ 262.0841, measured 262.0842.

Poly(methacryloylethyl phenylglyoxylate) (**Poly-1a**). To a stirring solution of 10% **1a** (w/w) in dry, thiophene-free benzene was added AIBN (0.5%, w/w with respect to **1a**). The solution was degassed by a stream of dry nitrogen before and during a 2 h period of reflux. The solution was then poured into 250 mL of methanol and the resulting precipitate was reprecipitated twice from methanol. Molecular weights as measured by GPC are $M_w = 27\,476$; $M_n = 9314$. DSC measurements revealed no T_g between 50 and 200 °C. It is expected that the T_g of this polymer is lower than room temperature because of its flexible backbone. The ^{1}H NMR spectrum shows no residual double bond in the polymer. Anal. Calcd: C, 64.11; H, 5.38. Found: C, 64.30; H, 5.48.

Cross-Linked Poly(methacryloylethyl phenylglyoxylate) (cross-linked Poly-1a). The precipitate resulting from the irradiation of **Poly-1a** in benzene was collected by filtration, washed three times with benzene, and dried. Anal. Calcd: C, 64.11; H, 5.38. Found: C, 64.40; H, 5.53.

Acryloylethyl Phenylglyoxylate (1b) was obtained in 89% yield by the same procedure outlined for **1a**. ^{1}H NMR (200 MHz) δ 4.48−4.53 (m, 2H), 4.62−4.68 (m, 2H), 5.85−5.91 (dd, $J_1 = 10.2$ Hz, $J_2 = 1.8$ Hz, 1H), 6.08−6.22 (dd, $J_1 = 17.6$ Hz, $J_2 = 10.2$ Hz, 1H), 6.41−6.50 (dd, $J_1 = 17.6$ Hz, $J_2 = 1.8$ Hz, 1H), 7.47−7.55 (m, 2H), 7.63−7.67 (m, 1H), 7.99−8.03 (m, 2H). ^{13}C NMR (50 MHz) δ 61.62, 63.41, 127.59, 128.79, 129.86, 131.56, 132.12, 134.92, 163.31, 165.51, 185.64. MS 55 (12.9), 77 (26.1), 105 (100), 188 (0.1).

Poly(acryloylethyl phenylglyoxylate) (Poly-1b) was obtained by the same procedure as **Poly-1a**. Molecular weights as measured by GPC are $M_w = 31\,848$; $M_n = 8456$. DSC measurements revealed no T_g between 50 and 200 °C. The ^{1}H NMR spectrum shows no residual double bond in the polymer. Anal. Calcd: C, 62.90; H, 4.87. Found: C, 62.82; H, 4.85.

Cross-Linked Poly(acryloylethyl phenylglyoxylate) (Cross-Linked Poly-1b). The precipitation resulting from the irradiation of **Poly-1b** in benzene was collected by filtration, washed three times with benzene, and dried. Anal. Calcd: C, 62.90; H, 4.87. Found: C, 62.92; H, 4.89.

Acknowledgment. Financial support from the National Science Foundation (NSF DMR-9013109) and the Office of Naval Research (Navy N00014-91-J-1921) are gratefully acknowledged. We thank Dr. George S. Hammond for valuable discussions.

CM9705911

---

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