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Preparation of 4-Vinylbenzil and Photochemical Properties of Its Homopolymer and Copolymer with Styrene

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ABSTRACT: When irradiated at >400 nm in air, pendant benzil groups of 1-phenyl-2-(4-vinylphenyl)-1,2-ethanedione/styrene (VBz/S) copolymer films are transformed almost quantitatively into benzoyl peroxide (BP) groups. Subsequent heating at 91°C converts the pendant benzoyl peroxide groups to esters and benzoic acid moieties, and there is significantly more cross-linking than main-chain cleavage. Irradiation of the VBz/S copolymer films at 366, 313, and 254 nm also results in formation of BP groups, but they are transformed in situ upon absorption of a second photon by the matrix. The ratios of the relative rate constants for BP formation and subsequent transformation upon absorption by a second photon decrease with decreasing wavelengths of radiation. Irradiation of a film composed of a nonmiscible intimate mixture of poly(1-phenyl-2-(4-vinylphenyl)-1,2-ethanedione) (PVBz) and polystyrene (PS) at >400 nm in air does not lead to discernible BP concentrations as well. Instead, the unreacted pendant benzil groups act as photosensitizers to transform the peroxy moieties almost immediately. In addition, we demonstrate that cross-linking of the VBz/S copolymer film, induced by 254 nm radiation, can be utilized to record a negative image.

Introduction

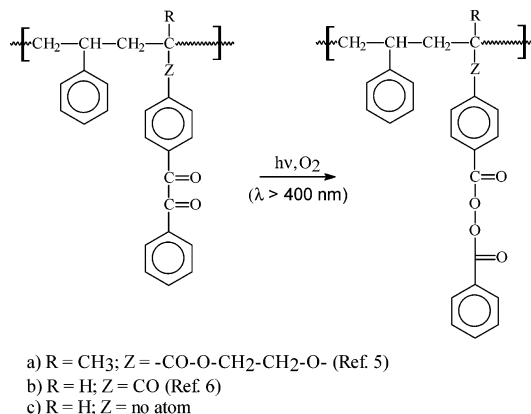
Benzil is an industrially important member of the class of molecules with 1,2-dicarbonyl functionality. It has been utilized in the preparation of photographic materials and polymer resists and as a photoinitiator in radical polymerizations.^{1–3} The solution-phase photochemistry of benzil has been investigated extensively, in both the presence and absence of molecular oxygen. When molecular oxygen is available, photooxidation of benzil in benzene leads to phenyl benzoate, benzoic acid, biphenyl, and a small amount of benzoyl peroxide (BP).⁴

In addition, we have demonstrated that benzil can be converted almost quantitatively to BP in aerated polymer films upon irradiation at >400 nm (i.e., the long wavelength edge of the $n \rightarrow \pi^*$ absorption band, where BP does not absorb).^{2,3} Covalently attached BP pendant groups have been formed also by irradiation of copolymer films of 1-[4-(2-methacroyloxyethoxy)phenyl]-2-phenyl-1,2-ethanedione-*co*-styrene⁵ and 1-phenyl-2-(4-propenoylphenyl)-1,2-ethanedione-*co*-styrene⁶ (Scheme 1).

Decomposition of pendant benzoyl peroxide groups can be an efficient method to effect cross-linking of polymer chains. In fact, even when irradiated at >400 nm in air at room temperature, a small part of the peroxide pendant groups is decomposed; films of both copolymers above become partially insoluble in organic solvents after irradiation.^{5,6} However, decomposition of low molecular weight peroxides, doped into polymer films like those of polystyrene, results in a net decrease in polymer molecular weight (i.e., chain scission is more important than chain cross-linking under these conditions).⁷

Cross-linking of 1-[4-(2-methacroyloxyethoxy)phenyl]-2-phenyl-1,2-ethanedione-*co*-styrene was presumed to

Scheme 1



emanate predominantly from easy radical abstraction of hydrogen atoms from the oxyethoxy ($-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$) groups.⁵ Cross-linking of (unheated) films of 1-phenyl-2-(4-propenoylphenyl)-1,2-ethanedione-*co*-styrene by >400 nm is thought to occur as a result of absorption by photons in the red edge of the n, π^* band of monocarbonyl groups and subsequent energy transfer to benzoyl peroxide groups.⁶

We report here our investigations of the photochemistry of copolymer films of a novel monomer, 4-vinylbenzil (VBz), and styrene (VBz/S). Heretofore, benzil pendant groups have been attached to polymer chains via 1-methacroyloxy-2-ethoxy⁵ and vinyl ketone⁶ tethers. The effect of abstractable H atoms of these tethers on cross-linking⁵ or how the carbonyl groups may modify the photochemical properties of the polymer films⁶ may be different for VBz/S and related copolymers. The VBz/S copolymer may exhibit a more regular distribution of benzil pendant groups along the polymer chains (vide infra), and, therefore, a more regular cross-linked network, than the related copolymers. Additionally, the absence of carbonyl groups, other than those associated

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with the benzil moiety or other groups that absorb in the infrared region where oxidative changes are easily diagnosed, should facilitate quantitative analyses of the photochemical and subsequent events.

Experimental Part

Instrumentation. IR spectra were recorded on a Nicolet 400 (Nicolet, Germany) FT spectrophotometer. UV/vis absorption spectra were measured on a SPECORD M40 (Carl Zeiss, Jena, Germany) spectrophotometer. Molecular weights were estimated by gel permeation chromatography (GPC) with THF (HPLC grade) as eluent, a PSS SDV 5 μ m column ($d = 8$ mm, $l = 300$ mm), a Waters 515 pump, and a Waters refractive index detector. The instrument was calibrated with PS standards. ^1H and ^{13}C NMR spectra were measured on Bruker AM 300 (Germany) and Varian VXR-300 (USA) spectrometers with TMS as internal standard. Differential scanning calorimetry (DSC) measurements were carried out on a Mettler-Toledo DSC 8211^e calorimeter that was calibrated for temperature and heat of fusion with indium.

Syntheses. Poly[1-(4-methacroyloxyethoxyphenyl)-2-phenyl-1,2-ethanedione] was available from previous investigations.⁸

1-(4-Ethylphenyl)-2-phenyl-1-ethanone (I). Phenylacetyl chloride (74.1 g, 0.48 mol) was added to a cooled (0 $^{\circ}\text{C}$), stirred suspension of anhydrous aluminum chloride (69.5 g, 0.52 mol) in carbon tetrachloride (290 mL). Then, ethylbenzene (55 g, 0.52 mol) was added dropwise at a rate that maintained the temperature below 5 $^{\circ}\text{C}$. Thereafter, the temperature was increased to 20 $^{\circ}\text{C}$, and the reaction mixture was poured onto a mixture of concentrated hydrochloric acid and ice, extracted with chloroform, dried with anhydrous sodium sulfate, and concentrated under vacuum. The crude product was distilled at 170–200 $^{\circ}\text{C}/15$ Torr and crystallized from ligroin to yield 67 g (62%); mp 59–61 $^{\circ}\text{C}$ (lit. mp 62–64 $^{\circ}\text{C}$).⁹

^1H NMR (CDCl_3): δ (ppm) 1.25 (t, $J = 7.5$ Hz, 3H, CH_3); 2.69 (q, $J = 7.8$ Hz, 2H, CH_2); 4.26 (s, 2H, CH_2); 7.30 (m, 7H, arom); 7.94 (d, $J = 8.1$ Hz, 2H, arom).

^{13}C NMR (CDCl_3): δ (ppm) 15.2 (CH_3); 28.9 (CH_2); 45.4 (CH_2); 126.8 (CH_{Ar}); 128.2 (CH_{Ar}); 128.6 (CH_{Ar}); 128.9 (CH_{Ar}); 129.4 (CH_{Ar}); 134.3 (C_{Ar}); 134.8 (C_{Ar}); 150.2 (C_{Ar}); 197.3 ($\text{C}=\text{O}$).

1-(4-Ethylphenyl)-2-phenyl-1,2-ethanedione (II). At room temperature, selenium dioxide (24 g, 0.21 mol) was added to a stirred solution of I (22.4 g, 0.1 mol) in 70% acetic acid (500 mL), and the mixture was stirred at 90–100 $^{\circ}\text{C}$ for 9 h. Almost all of the solvent was removed under reduced pressure, and the residue was placed in an aqueous sodium bicarbonate solution and extracted with benzene. The extract was dried with anhydrous sodium sulfate and concentrated under vacuum to give 22 g (90%) of an orange oil (one spot by silica gel thin-layer chromatography) that was used without additional purification (solid, mp 55 $^{\circ}\text{C}$,¹⁰ or a liquid, bp 170 $^{\circ}\text{C}/1$ Torr¹¹). ^1H NMR (CDCl_3): δ (ppm) 1.25 (t, $J = 7.6$ Hz, 3H, CH_3); 2.70 (q, $J = 7.6$ Hz, 2H, CH_2); 7.35 (d, $J = 8.2$ Hz, 2H, arom); 7.50 (m, 2H, arom); 7.65 (m, 1H, arom); 7.88 (m, 2H, arom); 7.97 (m, 2H, arom).

UV/vis ($\text{CHCl}_3/\text{MeOH}$): λ_{max} [nm] (ϵ [$\text{L mol}^{-1} \text{cm}^{-1}$]) 269/265 (45500/72900) and 394/375 (218/132).

1-[4-(1-Bromoethyl)phenyl]-2-phenyl-1,2-ethanedione (III). *N*-Bromosuccinimide (17.8 g, 0.1 mol) and 2,2'-azobis(2-methylpropionitrile) (AIBN; 0.225 g, 1.5 mmol) were added to a solution of II (22 g, 0.09 mol) in 80 mL of carbon tetrachloride. The reaction mixture was warmed slowly and allowed to reflux for 5 h. After cooling the mixture to ambient temperature, the solid (succinimide) was removed by filtration, and the filtrate was concentrated at reduced pressure to give 28 g (~100%) of crude product as an orange-red oil that was used without further purification.

^1H NMR (CDCl_3): δ (ppm) 2.02 (d, $J = 6.9$ Hz, 3H, CH_3); 5.18 (q, $J = 6.9$ Hz, 1H, CH); 7.48 (m, 2H, arom); 7.52 (m, 2H, arom); 7.65 (m, 1H, arom); 7.93 (m, 4H, arom).

UV/vis ($\text{CHCl}_3/\text{MeOH}$): λ_{max} [nm] (ϵ [$\text{L mol}^{-1} \text{cm}^{-1}$]) 272/270 (88800/125200) and 380/377 (93/109).

1-[4-(1-Acetyloxyethyl)phenyl]-2-phenyl-1,2-ethanedione (IV). A mixture of III (28 g, 0.09 mol) and anhydrous potassium acetate (53.5 g, 0.546 mol) was refluxed in 99% acetic acid (150 mL) for 4 h. The mixture was concentrated under reduced pressure, and the residue was added to aqueous sodium bicarbonate and extracted with diethyl ether. After drying (anhydrous sodium sulfate) and evaporation of the ether, 26 g (~100%) of crude product was obtained as a brown-red oil. It was used without further purification.

^1H NMR (CDCl_3): δ (ppm) 1.45 (d, $J = 6.6$ Hz, 3H, CH_3); 2.00 (s, 3H, CH_3COO); 5.80 (q, $J = 6.6$ Hz, 1H, CH); 7.39 (m, 2H, arom); 7.42 (m, 2H, arom); 7.60 (m, 1H, arom); 7.88 (m, 4H, arom).

UV/vis ($\text{CHCl}_3/\text{MeOH}$): λ_{max} [nm] (ϵ [$\text{L mol}^{-1} \text{cm}^{-1}$]) = 265/262 (104600/82100) and 378/376 (118/86).

1-[4-(1-Hydroxyethyl)phenyl]-2-phenyl-1,2-ethanedione (V). Aqueous sodium hydroxide (30 g in 30 mL of water) was added to a solution of IV (26 g, 0.09 mol) in methanol (300 mL). The mixture was stirred at room temperature for 15 min. After acidification with hydrochloric acid, the solid (salt) was removed by filtration, and the filtrate was concentrated under reduced pressure. The soluble portion of the residue was taken up in diethyl ether and yielded a red oil (23 g, ~100%) after removal of the ether under reduced pressure. It was eluted on a silica gel column with benzene initially to remove a small amount of impurities and with ethyl acetate to obtain the product as yellowish oil.

^1H NMR (CDCl_3): δ (ppm) 1.47 (d, $J = 6.5$ Hz, 3H, CH_3); 3.88 (s, 1H, OH); 4.95 (q, $J = 6.4$ Hz, 1H, CH); 7.48 (m, 2H, arom); 7.50 (m, 2H, arom); 7.75 (m, 1H, arom); 7.90 (m, 4H, arom).

UV/vis ($\text{CHCl}_3/\text{MeOH}$): λ_{max} [nm] (ϵ [$\text{L mol}^{-1} \text{cm}^{-1}$]) = 261/260 (65800/58500) and 375/375 (53/55).

1-Phenyl-2-(4-vinylphenyl)-1,2-ethanedione (VBz). Hydroquinone (0.1 g) and P_2O_5 (6 g, 15 mmol) were added to a solution of V (2 g, 8 mmol) in benzene (60 mL), and the mixture was stirred at room temperature for 3 h, filtered, and concentrated under vacuum. The product was isolated by column chromatography on silica gel with ligroin:benzene (4:1 \rightarrow 2:1) as eluent to yield 0.8 g (40%) of a liquid that was stored as a ligroin:benzene (3:1) solution in a refrigerator until being used. One spot by silica gel thin-layer chromatography and one peak by HPLC using a 250 \times 4 mm Separon SGX C18 column (Tessek Ltd. Prague, Czech Republic), UV detector LCD 254 (Laboratory equipments, Prague, Czech Republic), and 8:2 methanol:water as eluent.

^1H NMR (CDCl_3): δ 5.44 (d, $J_{\text{cis}} = 10.8$ Hz, 1H, CH_2); 5.91 (d, $J_{\text{trans}} = 17.4$ Hz, 1H, CH_2); 6.75 (2d, $J_{\text{cis}} = 11.1$ Hz, $J_{\text{trans}} = 17.7$ Hz, 1H, CH); 7.52 (m, 4H, arom); 7.65 (m, 1H, arom); 7.93 (m, 2H, arom); 7.97 (m, 2H, arom).

^{13}C NMR (CDCl_3): δ (ppm) 118.0 (CH_2); 126.7 (CH); 129.0 (CH_{Ar}); 129.9 (CH_{Ar}); 130.3 (CH_{Ar}); 132.1 (C_{Ar}); 133.0 (C_{Ar}); 134.9 (CH_{Ar}); 135.7 (CH_{Ar}); 143.9 (C_{Ar}); 194.0 ($\text{C}=\text{O}$); 194.5 ($\text{C}=\text{O}$).

UV (CCl_4): λ_{max} [nm] (ϵ [$\text{L mol}^{-1} \text{cm}^{-1}$]) = 294 (100000) and 400 (88).

Mass m/e : 236 (M^+ , 10%), 131 ($\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{CO}$, 90%), 105 (PhCO , 36%), 103 ($\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4$, 30%), 77 (Ph , 100%).

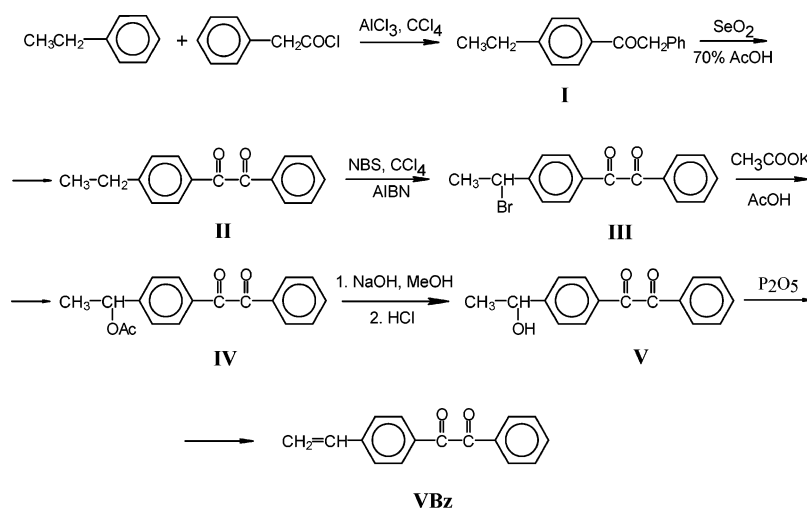
Poly[1-Phenyl-2-(4-vinylphenyl)-1,2-ethanedione] (PVBz). The homopolymer was prepared by allowing a neat sample of VBz to remain in a refrigerator for 2 weeks. It was precipitated three times from chloroform solution into methanol. By GPC analysis using PS standards for calibration, $M_w = 1\,221\,000$ and $M_n = 33\,500$.

Elemental analysis calcd for $\text{C}_{16}\text{H}_{13}\text{O}_2$: C 81.34%; H 5.12%. Found: C 81.12 \pm 0.14%; H 5.13 \pm 0.01%.

^1H NMR (CDCl_3): δ 1.60 (b (broad peak), 2H, CH_2); 2.00 (b, 1H, CH); 6.61 (b, 2H, arom *o*-CH); 7.47 (b, 2H, arom *m*-C=O); 7.60 (b, 3H, arom *p*-C=O and *m*-CH); 7.89 (b, 2H, arom *o*-C=O).

^{13}C NMR (CDCl_3): δ (ppm) 41.2 (CH); 41.3 (CH_2); 127.4 (CH_{Ar}); 128.0 (CH_{Ar}); 129.1 (CH_{Ar}); 130.0 (CH_{Ar}); 131.3 (C_{Ar}); 132.8 (C_{Ar}); 135.0 (CH_{Ar}); 151.5 (C_{Ar}); 193.4 ($\text{C}=\text{O}$); 194.1 ($\text{C}=\text{O}$).

Scheme 2



Poly[1-phenyl-2-(4-vinylphenyl)-1,2-ethanedione-co-styrene] (VBz/S). An ampule containing 0.5 g of VBz, 8.8 g of styrene, and 20 mg of AIBN was sealed under argon and polymerized at 59 °C for 12 h. The copolymer was precipitated three times from chloroform solution into methanol to yield 4.8 g (51.6 wt %) of a slightly yellowish polymer. From the ratio of integrated peak areas of the aromatic hydrogens in the ^1H NMR spectrum (chloroform- d), the VBz content was 10.4 wt %; estimates from elemental analysis (see below) are 10.1 ± 1.8 wt % (carbon) and 9.4 ± 1.0 wt % (hydrogen). By GPC analysis (PS calibration), $M_w = 216\,000$ and $M_n = 113\,000$. By DSC, $T_g = 107.7$ °C.

Elemental analysis: C $91.15 \pm 0.19\%$; H $7.49 \pm 0.04\%$.

^1H NMR (CDCl_3): δ 1.45 (b, CH_2 of S), 1.86 (b, CH of S and CH_2 of VBz), 2.07 (b, CH of VBz), 6.50 (b, 2H-arom of S and 2H-arom of VBz), 7.08 (b, 3H-arom of S), 7.54 (b, 3H-arom of VBz), 7.66 (b, 2H-arom of VBz), 8.00 (b, 2H-arom of VBz).

^{13}C NMR (CDCl_3): δ (ppm) 40.5 (CH), 43.6 (CH_2), 125.6 (CH_{Ar} of S), 127.6 (CH_{Ar} of S and CH_{Ar} of VBz), 127.9 (CH_{Ar} of S and CH_{Ar} of VBz); 129.0 (CH_{Ar} of VBz); 129.7 (CH_{Ar} of VBz); 130.7 (C_{Ar} of VBz), 133.1 (C_{Ar} of VBz); 134.8 (CH_{Ar} of VBz), 145.3 (C_{Ar} of S), 194.3 ($\text{C}=\text{O}$), 195.2 ($\text{C}=\text{O}$). Note that no quaternary C_{Ar} signal was observed although it was detected in the spectrum of PVBz at 151.5 ppm.

Irradiations and Measurements. Films (10 cm^2 area) consisting of 40 mg of copolymer (VBz/S), 4 mg of homopolymer PVBz in 16 mg of PS, and 4 mg of poly[1-(4-methacroyloxyethoxyphenyl)-2-phenyl-1,2-ethanedione] in 16 mg of PS were prepared from solution as described^{2,3} and irradiated at ambient temperature through a UV CL SR HPR plastic film filter (LLumar) at >400 nm in a Spectramat (Ivoclar A.G., Schaan, Liechtenstein) apparatus (350–530 nm). A homemade “merry-go-round” apparatus was employed in some experiments. It consists of three concentric quartz walls in which a 125 W medium-pressure mercury arc is in the inner cylinder and is surrounded by a layer of cooling water and a 1 cm thick layer of a liquid filter (optional). The distance of each sample (placed in rotating holder) from arc is about 9 cm. The radiation was filtered with a 4 mm Corning 5860 glass filter (for 366 nm) or a 1 cm thick layer of aqueous potassium chromate (0.3884 g dm^{-3}) and sodium carbonate (50 g dm^{-3}) in combination with a 0.5 cm Corning glass filter N 7-59 (9863) (for 313 nm). For irradiations at mainly 254 nm, films were mounted in the “merry-go-round” apparatus, and the lamp was a low-pressure mercury arc (TNK 6/20, Hanau GmbH, Germany). Thermal decompositions of benzoyl peroxide groups in irradiated films were conducted in air at 91 ± 1 °C in the column oven of a Shimadzu gas chromatograph.

The photolithography experiments employed the low-pressure mercury arc. A lithographic mask on a quartz glass was placed over a silicon wafer with a spin-surface coated VBz/S film (ca. 0.5 μm thickness), made from a chloroform solution.

The postirradiated image was developed by placing the film in isobutyl methyl ketone.

Results and Discussion

Synthesis of 4-Vinylbenzil. 4-Vinylbenzil was prepared in six steps (Scheme 2), the first five of which, yielding 1-[4-(1-hydroxyethyl)phenyl]-2-phenyl-1,2-ethanedione (**V**), have been described previously for the similar compounds.¹² Compounds **II–IV** are high boiling liquids that were prepared in nearly quantitative yields. Because they are difficult to purify by chromatographic methods, they were used in crude form, and only intermediate **V** and VBz were purified by chromatography. The final step, dehydration of **V**, was attempted with various reagents including triphenylphosphine in CCl_4 ,¹³ POCl_3 in pyridine,¹⁴ BF_3OEt_2 in dichloromethane,¹⁵ FeCl_3 on silica gel,¹⁶ and *p*-toluenesulfonic acid in benzene.¹⁷ Unfortunately, low yields of the desired product, contaminated with byproducts, were achieved in most cases. In addition, significant amounts of polymer, perhaps from the desired VBz, were also detected. VBz was finally prepared in 40% yields by dehydration with P_2O_5 in benzene¹⁸ at room temperature (Scheme 2).

Syntheses of 4-Vinylbenzil Homopolymer and VBz/S Copolymer and Their Characterization. Both PVBz and VBz/S are high molecular weight polymers. PVBz, owing to its polymerization without added initiator, has a broad molecular weight distribution. The polydispersity of the VBz/S, prepared by polymerization initiated with AIBN, is near the theoretical value. In the monomer mixture, VBz reacts faster than styrene. Therefore, the average content of VBz units in the copolymer (4.9 mol % at 51.6 wt % conversion) is higher than in the monomer mixture (2.44 mol %). From the contents of the monomer units in the monomer mixture and in the polymers, as well as from additional information in the literature^{8,19} and those presented here, the distribution of benzil groups attached to main chains by different tethers in copolymers with styrene cannot be discerned precisely. It is only possible to conclude that the VBz polymerizes with styrene equally fast or faster than monomers with very reactive vinyl ketone and methacroyl tethers! Therefore, the distribution of VBz units in the styrene copolymer is similar to or somewhat less regular than the previously prepared copolymers. On the basis of comparisons

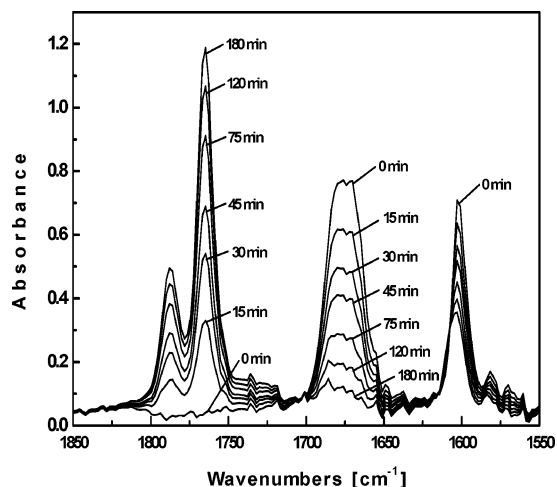


Figure 1. FT-IR spectra of a VBz/S copolymer film irradiated at >400 nm in a Spectramat apparatus at RT in air for various periods.

with published data,²⁰ it follows that the copolymerizing properties of VBz are similar to those described for copolymerization of unsubstituted styrene and styrene with strongly deactivating substituents at the para position. Owing to the copolymerization properties, the content of VBz structures in the VBz/S copolymer formed at the beginning of polymerization is higher than at the end of the reaction. Despite the chemical inhomogeneities of the VBz/S copolymer, the prepared films are perfectly transparent, and most probably VBz groups are distributed regularly throughout the sample.

Photochemical Generation of Benzoyl Peroxide Groups in VBz/S (Molar Ratio 5:95) Copolymer Films. Conversions of pendant benzil groups during irradiations of VBz/S at >400 nm and ambient temperature were followed by FT IR spectroscopy. As reaction progressed, the intensity of the characteristic IR stretching band of the 1,2-dicarbonyl groups at $1660\text{--}1690$ cm^{-1} decreased, and their nearly quantitative transformation to benzoyl peroxide (BP) groups was complete after 3 h (Figure 1, Scheme 1). Formation of the BP groups is accompanied in IR spectra by the growth of new intense bands in the $1750\text{--}1800$ cm^{-1} region.² The nearly quantitative transformation was also indicated by the very similar pseudo-first-order rate constants for loss of benzil groups ($k = 0.98$ h^{-1} , obtained from plots of the log of the decrease of absorbance at 1675 cm^{-1} vs time) and formation of BP groups ($k = 1.04$ h^{-1} , from plots of the log of the increase of absorbance at 1766 cm^{-1} vs time).

UV-vis absorption spectra were also recorded in the region of the diketone $n \rightarrow \pi^*$ absorption band (~ 390 nm) during irradiation ($\lambda > 400$ nm) of VBz/S films (Figure 2). There is a continuous decrease in absorbance at 390 nm, and only the tail of a stronger $\pi \rightarrow \pi^*$ band is detectable after 3 h of irradiation.

It was possible to monitor the formation of peroxides in a VBz/S copolymer film in deuteriochloroform by ^{13}C NMR spectroscopy. A VBz/S film was irradiated at >400 nm and ambient temperature to about 70% conversion of the 1,2-dicarbonyl groups (to yield peroxides). The spectrum included a strong new peak at 163.1 ppm attributed to the peroxide and residual peaks at 194.3 and 194.7 ppm from the unreacted 1,2-dicarbonyl groups.

Copolymer films were irradiated also at 366 , 313 , and 254 nm to investigate influence of wavelength on their

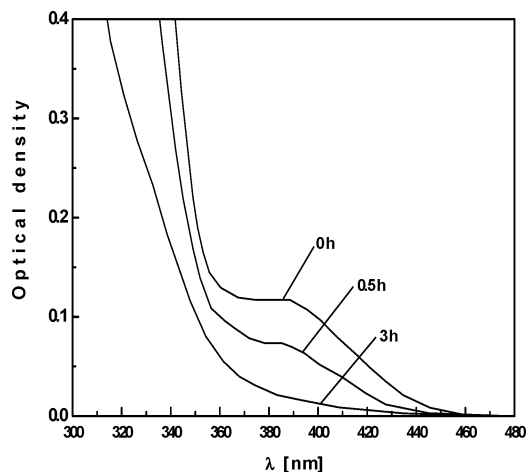


Figure 2. UV-vis absorption spectra of a VBz/S copolymer film irradiated at >400 nm in a Spectramat apparatus at RT in air for various periods.

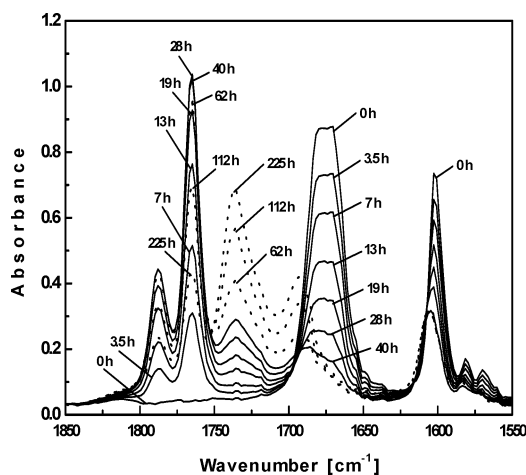


Figure 3. FT-IR spectra of a VBz/S copolymer film irradiated at 366 nm at RT in air for various periods in a merry-go-round apparatus.

photochemical properties. Although formation of the BP groups was observed also during irradiation of VBz/S copolymer films at 366 nm (Figure 3), FT IR spectra indicate that the peroxides were converted slowly to esters (growth of peaks in the $1700\text{--}1750$ cm^{-1} region) and benzoic acid (growth of peaks in the $1670\text{--}1700$ cm^{-1} region). It is possible to fit the temporal intensity changes of the 1766 cm^{-1} band in Figure 3 (dotted spectrum) to an exponential function and calculate a pseudo-first-order rate constant for decomposition of BP groups (8.5×10^{-3} h^{-1}) that is considerably smaller than the one for their formation (5.9×10^{-2} h^{-1}), based on the decreases of absorbance of 1,2-diketone groups at 1675 cm^{-1} . For this reason, the intensities of absorbance bands from the peroxide increase up to 90% benzil conversion and decrease only when concentration of benzil groups becomes very small. After 40 h of irradiation, only conversion of peroxides can be detected (Figure 3, dotted spectra). This experiment also shows that the decomposition of the peroxides is due principally to their small absorption at 366 nm and not by sensitization (energy transfer) from the remaining benzil groups. Although a sensitization mechanism was operative in the PVBz and poly[1-(4-methacroyloxyethoxyphenyl)-2-phenyl-1,2-ethanedione] homopolymers (see below), it is not here because the concentration of 1,2-dione groups is much smaller, their average separa-

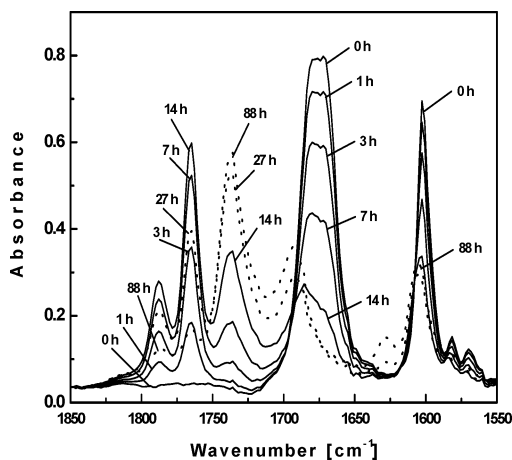


Figure 4. FT-IR spectra of a VBz/S copolymer film irradiated at 313 nm at RT in air for various periods in merry-go-round apparatus.

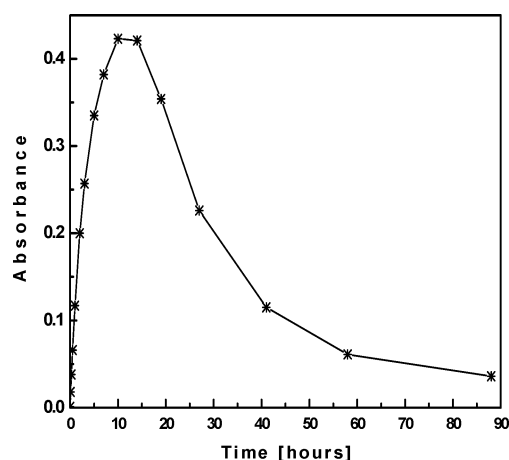


Figure 5. IR absorbance changes at 1766 cm^{-1} (from Figure 4) in a VBz/S copolymer film vs time of irradiation ($\lambda = 313$ nm) at RT in air.

tion is much larger, and they are more randomly distributed in VBz/S than in the PVBz and poly[1-(4-methacroyloxyethoxyphenyl)-2-phenyl-1,2-ethanedione]-homopolymers. As a result, the distance between VBz donors and peroxide acceptors formed in the glassy matrix provided by VBz/S is too large for efficient energy transfer.

Irradiation of VBz/S at ambient temperature with 313 nm radiation leads also to the in situ transformation of benzil to BP groups (Figure 4). As expected from the molar extinction coefficients of the species involved (Figure 2), the ratio (R) of the relative pseudo-first-order rate constants for formation and subsequent transformation of BP groups, as calculated from the temporal changes in the relevant IR bands (vide ante), is smaller with 313 nm radiation ($R = 0.11 \text{ h}^{-1}/0.045 \text{ h}^{-1}$ or <3) than with 366 nm radiation ($R \approx 7$). For this reason, the peroxide absorbance increases up to only ca. 70% conversion of benzil groups at 313 nm (Figures 4 and 5) vs ca. 90% conversion at 366 nm. After ca. 20 h of irradiation at 313 nm, only loss of peroxides can be observed.

No absorptions attributable to BP groups could be discerned in FT IR spectra of a VBz/S copolymer film irradiated principally at 254 nm (Figure 6). We believe that transformation of benzil to BP groups is still the major reaction pathway, but photoinduced decomposition of BP groups proceeds more rapidly than they are

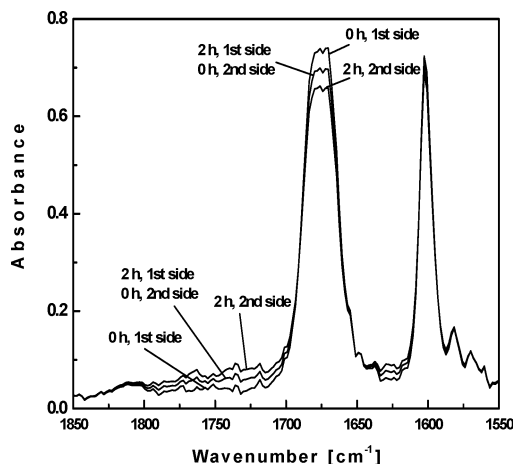


Figure 6. FT-IR spectra of a VBz/S copolymer film irradiated at 254 nm at RT in air for various periods.

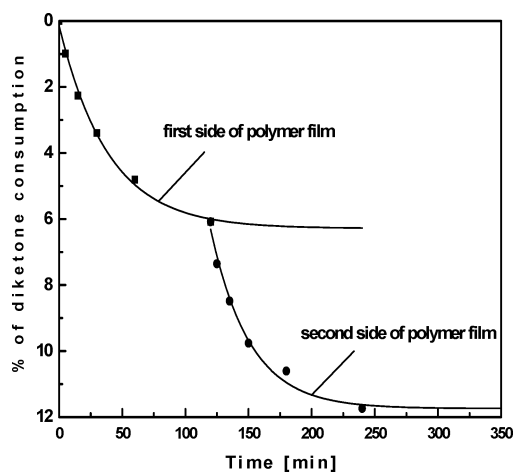
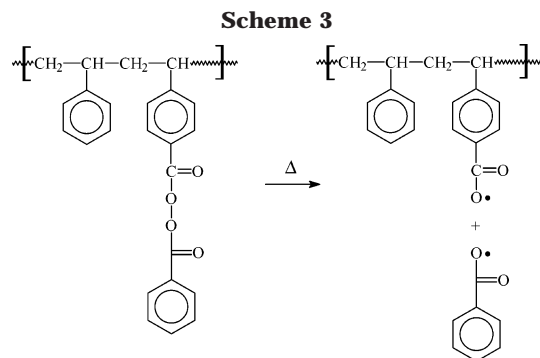


Figure 7. Dependence of diketone consumption on time of irradiation ($\lambda = 254$ nm) in a VBz/S copolymer film at RT in air. See text for details.

formed. The 254 nm wavelength region corresponds to the strong aromatic $\pi \rightarrow \pi^*$ absorptions. As a result of the high optical densities in this region, radiation penetrates primarily the parts of the film near the surface, and the remainder of the film is not exposed to large photon fluxes. As a result, only about 12% (6% on each exposed side) of the benzil groups are converted to peroxides after protracted irradiation periods (Figure 7). If it is assumed reasonably that only those benzil groups near the film surfaces react, the depth of penetration of the radiation (and the space of reaction) is limited to only about $2.4 \mu\text{m}$ (i.e., 6% of the total $40 \mu\text{m}$ thickness). Consistent with this assumption, the pseudo-first-order rates for benzil consumption on each side are the same within experimental error.

Thermal Decomposition of Photochemically Generated Benzoyl Peroxide Groups in VBz/S Copolymer Films. Thermal decomposition (at 91°C ; Scheme 3) of BP groups, generated by prior irradiation of VBz/S copolymer films at >400 nm (Figure 1), was followed by IR spectral changes in the regions of the peroxide (decreases at $1750\text{--}1800 \text{ cm}^{-1}$), ester (increases at $1700\text{--}1750 \text{ cm}^{-1}$), and benzoic acid (increases at $1670\text{--}1700 \text{ cm}^{-1}$) absorbances (Figure 8).

The first-order rate constant for thermal decomposition of BP groups, $k_t = 0.08 \text{ h}^{-1}$, was calculated from IR peak intensity changes at $1750\text{--}1780 \text{ cm}^{-1}$. Recently, we noted⁶ that the rate constants for thermal decom-



position of low molecular weight BP derivatives in PS as well as two different BP pendant groups of copolymers are larger when there is an electron-donating substituent at the 4-position of one of the aromatic rings than when the substituent is electron-withdrawing. Although the BP groups generated photochemically in the VBz/S copolymer contain an electron-donating substituent, their k_t value is comparable to that of the BP group with an electron-withdrawing substituent (i.e., from the irradiated copolymer of 1-phenyl-2-(4-propenoylphenyl)-1,2-ethandione and styrene; Table 1).

Other factors besides the electronic nature of the substituents must influence the rates of BP thermolyses in styrene copolymers. In this regard, it is important to note that k_t (and its associated rate) is not a simple process. What is measured is the net loss of BP groups with time—the difference between the total number of peroxy bonds lysed and the number of radical pairs that combine to re-form BP groups. This difference can be mediated by the ability of the “walls” of the cages²¹ to act as hydrogen atom donors to trap one (or both) of the radicals in an intimate pair. Thus, the relatively high rate of BP decomposition in irradiated 1-{4-(2-methacroyloxyethoxy)phenyl}-2-phenyl-1,2-ethanedione/styrene copolymer⁵ may be related to the presence of relatively easily abstractable hydrogen atoms from the $-O-CH_2-CH_2-O-$ tether segments.

Also, the local flexibility of groups constituting the “cage” environment of the BP groups may be important to the overall rates. Factors such as “hole” free volume, the length and nature of the tether between the BP group and its the main chain, and, to a lesser extent, the number of degrees under the glass transition the thermolysis is conducted must contribute to the overall flexibility. In fact, flexibility affects the rate of cleavage of the peroxy linkages of the BP groups as well as the rates at which the intimate radical pairs recombine.²¹ Of these factors, only the length of the tethers differ significantly among the copolymers with styrene.

Cross-Linking of a VBz/S Copolymer Film. In principle, benzoyloxy radicals from oxidized, low molecular weight benzil dopants or from BP groups appended to polymer chains can abstract a hydrogen atom from the polymer, add to a phenyl ring (of a polystyrene polymer or copolymer), recombine, or disproportionate. The latter two reaction pathways have no influence on the average molecular weight or degree of cross-linking of the polymer. The former two pathways can influence both the average molecular weight and the degree of cross-linking, depending on the nature of the benzoyloxy radical.

For instance, thermolysis of each pendant diacyl peroxide group of irradiated 1-[4-(2-methacroyloxyethoxy)phenyl]-2-phenyl-1,2-ethanedione/styrene⁵ and 1-phenyl-2-(4-propenoylphenyl)-1,2-ethanedione/styrene⁶ produces one “free” and one polymer-bound acyloxy radical.

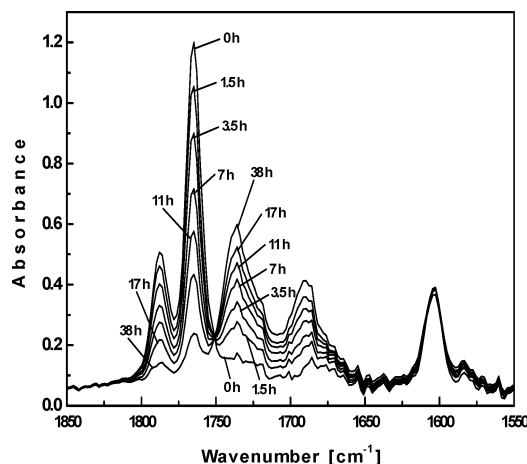
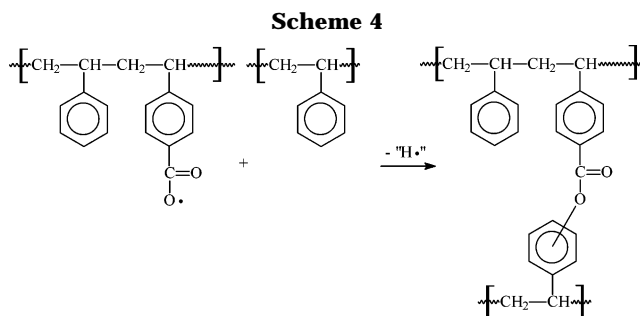


Figure 8. Changes in the FT-IR spectra of the region of BP group absorbances at 91 °C in a VBz/S copolymer film that had been preirradiated at >400 nm at RT in air (Figure 1).

Table 1. First-Order Rate Constants at 91 °C for Thermal Decomposition (k_t) of Various Types of Pendant Benzoyl Peroxide Structures Generated by Irradiation of Benzil Containing Copolymer Films

benzoyl peroxide source and carrier	k_t (h ⁻¹)
VBz/S	0.08
1-{4-(2-methacroyloxyethoxy)phenyl}-2-phenyl-1,2-ethanedione- <i>co</i> -styrene	0.256 ⁵
1-phenyl-2-(4-propenoylphenyl)-1,2-ethanedione- <i>co</i> -styrene	0.077 ⁶



yl-2-(4-propenoylphenyl)-1,2-ethanedione/styrene⁶ produces one “free” and one polymer-bound acyloxy radical. Cross-linking initiated by the polymer-bound radical (Scheme 4) was evidenced by the insolubility of these polymers in common solvents after being heated. However, thermolysis of a low-molecular-weight BP-containing molecule doped in PS resulted in a reduction in polymer chain lengths and no insoluble fraction.⁷ In this case, neither of the benzoyloxy radicals is covalently attached to the polymer chains. Their abstraction of a hydrogen atom from the polymer backbone favors chain scission, and addition to a pendant phenyl ring does not result in cross-linking.

It is known that the reverse of the addition reaction of benzoyloxy radicals to a variety of aromatic rings (n.b., Scheme 4), including to styrene monomer, is extremely fast.^{22–24} Despite that, decomposition of benzoyl peroxide molecules in PS films leads the addition of benzoyloxy,⁷ as it does when our peroxidized copolymer is heated or irradiated. The reason for the additions to the aromatic rings is related to the high concentration of molecular oxygen in the films, presumed to be higher than in solutions of benzene or toluene (where similar phenomena occur^{23,24}). Molecular oxygen can remove a hydrogen atom at the *ipso* carbon of addition at a rate

that is at least comparable to the rate of the reverse addition of benzoyloxy from the intermediate.

The structures of the reaction sites (junction points) were investigated by ^{13}C NMR spectroscopy. A VBz/S film that had been irradiated at >400 nm and ambient temperature to about 70% conversion of the 1,2-dicarbonyl groups was heated to decompose ca. 50% of the so-formed peroxides. This procedure corresponds to about 1.5 mol % (based on monomer structure units) of reaction sites. Because of reactions not leading to cross-linking, especially the formation of carboxylic acids, the concentration of cross-linking sites is <1 mol %. The film was swollen in deuteriochloroform in a 1 cm tube for 2 days, and FIDs from it were accumulated for 70 h to obtain a spectrum with good signal-to-noise ratios. It contained a small peak ascribed to peroxide carbonyls at 163.12 ppm and larger peaks from 1,2-dicarbonyl groups at 194.29 and 194.7 ppm. However, no peaks due to the ester groups were detected, presumably because of the long relaxation times of the carbon atoms near cross-linking sites. Moreover, the formed ester structures are probably a mixture from *o*-, *m*-, and *p*-substitution on polystyrene phenyl rings. For these reasons, we are unable to estimate the fraction of peroxide groups that result in cross-links when they undergo thermal decomposition.

Prior to irradiation, VBz/S can be dissolved completely in chloroform and several other solvents at room temperature. However, even without heating, only ca. 25% remained soluble in chloroform after a film was irradiated at >400 nm until all of the benzil groups had been oxidized to BP moieties. After thermal decomposition of BP groups, the same film became completely insoluble in chloroform. Complete insolubility in chloroform was also achieved after irradiation of VBz/S films at 366 nm for 228 h or at 313 nm for 88 h without heating. In the IR spectra of Figures 3, 4, and 8, the absorbances associated with benzoic acids are about half as intense as those of the esters, the groups probably responsible for the cross-links. In these cases, as well as those in which the benzil chromophore is bound to the main chain by different tethers,^{5,6} aromatic ester formation should be an important process for cross-linking with styrene.

Protracted irradiation of a VBz/S copolymer film at 254 nm resulted in much more film insolubility (about 22%) than conversion of benzil moieties (about 12%). The very long chains of the polymer need few cross-links to become insoluble, even when long chain segments (lying deeper than the regions of radiation penetration and benzil reaction in the film) are completely free of cross-links.

Photooxidation of PVBz Homopolymer. As a comparison, the photooxidation of pendant benzil groups of the PVBz homopolymer was examined also as an admixture with polystyrene. Since the two polymers are immiscible, the vast majority of benzil groups are in an environment that approximates that of neat PVBz films. Polystyrene was added because the neat PVBz films could not be made sufficiently thin for the progress of the reactions to be followed by IR spectroscopy.

Irradiation of the mixed polymer film at >400 nm led to a decrease in absorbances in the 1650–1690 cm^{-1} region where benzil bands are found (Figure 9). However, the loss of benzil was accompanied by the appearance of a weak peroxide absorbance at 1750–1800 cm^{-1} . Instead, the absorbances associated with ester and acid

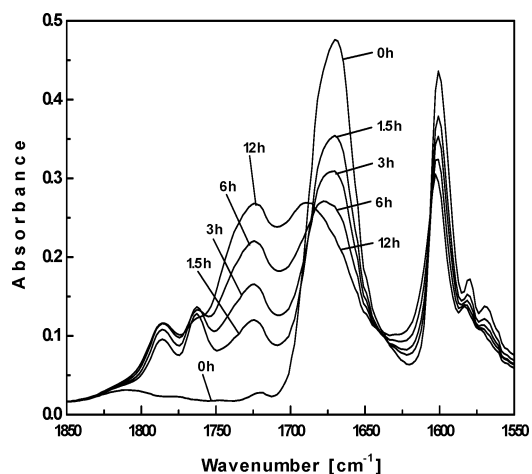


Figure 9. FT-IR spectra of a polymer film containing an admixture of 4 mg of homopolymer PVBz and 16 mg of PS irradiated at >400 nm in a Spectramat apparatus at RT in air for various periods.

groups in the regions 1710–1750 and 1650–1710 cm^{-1} increased a great deal. These results are in stark contrast to those found upon irradiation at >400 nm of VBz/S copolymer films (*vide ante*). Instead of the BP groups being stable, as they were to >400 nm radiation in the VBz/S copolymer, they react rapidly in the PVBz homopolymer. This comportment appears to be general for homopolymers containing pendant benzil groups because irradiations at >400 nm of an admixture of poly-[1-(4-methacroyloxyethoxyphenyl)-2-phenyl-1,2-ethanedi-one] in PS film produced changes in the IR spectra like those in the PVBz–polystyrene mixture.

The conversion of the as-formed BP groups in the homopolymers appears to be due to energy transfer from excited triplet states of the remaining benzil groups ($E_T = 53.4$ kcal mol^{-1}).²⁵ They possess more than sufficient energy to cleave $-\text{O}-\text{O}-$ bonds of the BP groups ($E_D \sim 33$ kcal mol^{-1}).²⁶ At the very high local concentrations of donors and acceptors, the energy transfer must be very efficient. The results demonstrate also that the polystyrene is segregated from the aggregated chains of the PVBz and PBzMA homopolymers and that stable BP groups can be made photochemically from benzil groups only in copolymers in which the second monomer is in excess.

Formation of a Negative Tone Image in the VBz/S Copolymer. As shown in Figure 6, irradiation of VBz/S copolymer at 254 nm leads to formation of a ca. 2 μm film layer that is highly cross-linked and, consequently, insoluble in all solvents examined. To determine the feasibility of employing VBz/S as a photoresist (i.e., to form nonerasable images), it was spin-coated as ca. 0.5 μm thick films onto silicon wafers from a chloroform solution. Then, 254 nm radiation was passed through a mask that was placed atop a quartz plate over the samples for 1, 2, and 10 min periods. Finally, the unirradiated parts were dissolved in isobutyl methyl ketone to develop the images. Although the experiments were not optimized for sensitivity or resolution, the pattern after 10 min irradiation contained features as narrow as 12 μm (Figure 10), comparable in size to the smallest apertures in the mask. Although the photoresists commonly employed industrially are based on photoacid- or photobase-amplified reactions that result in image formation in aqueous bases,^{27,28} the

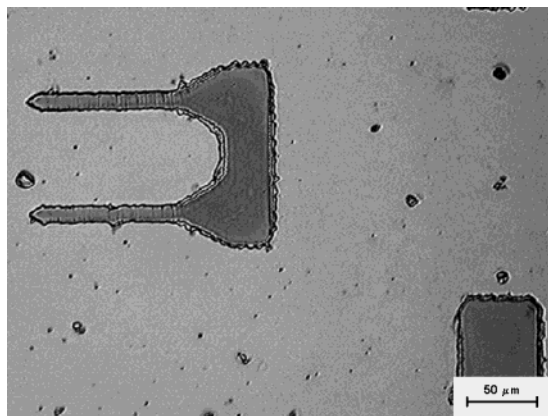


Figure 10. Developed images in a VBz/S copolymer film supported on a silicon wafer achieved after 10 min of irradiation at 254 nm through a mask.

VBz/S copolymer may fill a niche for specialized applications.

Conclusions

We have demonstrated that poly(4-vinylbenzil) and a copolymer of 4-vinylbenzil with styrene undergo efficient peroxidation of the 1,2-dicarbonyl functionality when their films are irradiated in air. Depending upon the wavelength of irradiation, the conversion dicarbonyl to peroxy moieties can be nearly quantitative (at >400 nm), or they can undergo subsequent in situ reactions involving the cleavage of the peroxy bonds and net cross-linking of polymer chains (at shorter wavelengths). The reactions can be mediated by controlling the density of 1,2-dicarbonyl groups; greater spatial dispersion attenuates photosensitized decompositions of peroxy groups. Finally, the ability of these polymers to form images when irradiated at 254 nm through a mask has been demonstrated. In addition, we expect that these polymers or variants of them will find applications in areas where controlled cross-linking or decomposition is desired.

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