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Photochemical Transformation of Benzil Carbonyl Pendant Groups in Polystyrene Copolymers to Benzoyl Peroxide Carbonyl Moieties and the Consequences of Their Thermal and Photochemical Decomposition

Jaroslav Mosnáček,[†] Richard G. Weiss,[‡] and Ivan Lukáč*,[†]

Polymer Institute, Slovak Academy of Science, Dúbravská cesta 9, 842 36 Bratislava, Slovak Republic, and Department of Chemistry, Georgetown University, Washington, DC 20057-1227

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ABSTRACT: When irradiated at >400 nm in air, the benzil carbonyl groups (BZG) of 1-phenyl-2-(4-propenoylphenyl)-1,2-ethanedione/styrene (PCOCO/S) copolymer films are transformed almost quantitatively to benzoyl peroxide carbonyl groups (BPG). Subsequent additional irradiation (at 366 nm) or heating (at 91 °C) of the BPG-containing copolymer films generates ester moieties, and significantly more cross-linking than main-chain cleavage is manifested in the copolymer. At 91 °C, the rate of the thermal decomposition of the pendant BPG is 3 times slower than that of noncovalently attached benzoyl peroxide molecules in polystyrene films.

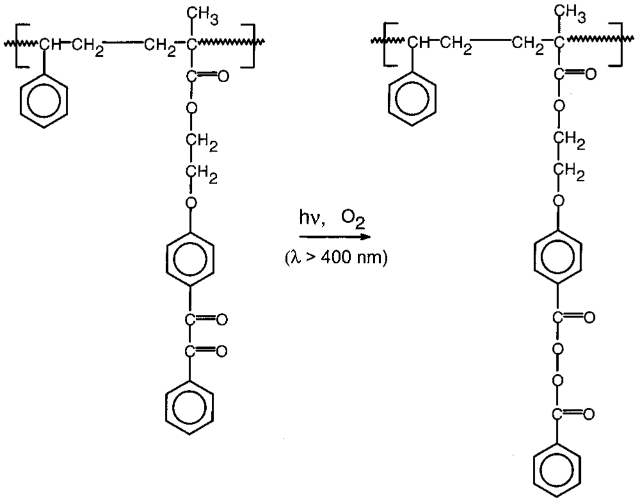
Introduction

Benzil (BZ) 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 BZ has been investigated extensively, in both the presence and absence of molecular oxygen. The main photochemical reaction of BZ triplets in the absence of oxygen is abstraction of a hydrogen atom,[4,5] leading to ketyl radicals from BZ and radicals from the hydrogen donor. Because of a lack of easily abstractable H atoms in oxygen-free solutions of benzene, BZ is photochemically inert. When molecular oxygen is available, photooxidation of BZ in benzene leads to phenyl benzoate, benzoic acid, biphenyl, and a small amount of benzoyl peroxide (BP).[6]

Recently, we reported that BZ can be converted almost quantitatively to BP in aerated polymer films by irradiation at >400 nm (i.e., the long wavelength edge of the n → π* 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-methacroyloxy)ethoxyphenyl]-2-phenyl-1,2-ethanedione/styrene in air[7] (Scheme 1). Thermal decomposition of BP in solid polymer matrices has been investigated as a means to generate primary radicals for cross-linking, grafting, selective degradation, bleaching, etc.[8]

The photochemistry (366 nm) of films of 1-phenyl-2-(4-propenoylphenyl)-1,2-ethanedione/styrene (PCOCO/S) copolymers (that are structurally similar to the copolymer bearing benzil groups in Scheme 1, but lack methacrylate groups and contain an additional carbonyl group) has been investigated previously in benzene in the presence and absence of molecular oxygen.[9] In the presence of oxygen, the 1,2-dione groups yield several low-molecular-mass products, including phenyl benzoate, biphenyl, benzoic acid, and polymeric species. The extent of formation of low molecular-mass products and the degree of attendant main-chain scission were very dependent on the availability of molecular oxygen, and no BP pendant groups were detectable by FT-IR spectroscopy.[9]

Scheme 1



The very different photochemical courses of BZ in solutions or polymer films[2,3,7] prompted us to investigate the photochemistry of the PCOCO/S copolymer in its film state. We find that carbonylated benzoyl peroxide groups (BPG) are formed efficiently upon irradiation at >400 nm in air (Scheme 2). Subsequently, they can be decomposed photochemically or thermally and utilized for grafting, cross-linking, or selective degradation.

Experiment Part

Materials. PCOCO/S copolymer (M_w = 981 000, M_n = 481 000; containing 25 wt % PCOCO),[7] poly[4-acetylphenyl-(vinyl)ketone],[10] and poly[phenyl(vinyl)ketone][11] were prepared as described. Benzoyl peroxide (Merck) was precipitated from chloroform into methanol. Polystyrene (PS) (Vestyron N, Hüls, Germany), chloroform, and benzene were analytical grade and used as received.

Irradiations and Measurements. Films consisting of 20 mg of PCOCO/S (10 cm^2 area) were prepared as described[2,3]

[†] Slovak Academy of Science.
[‡] Georgetown University.
* Corresponding author: e-mail upolluka@savba.sk.

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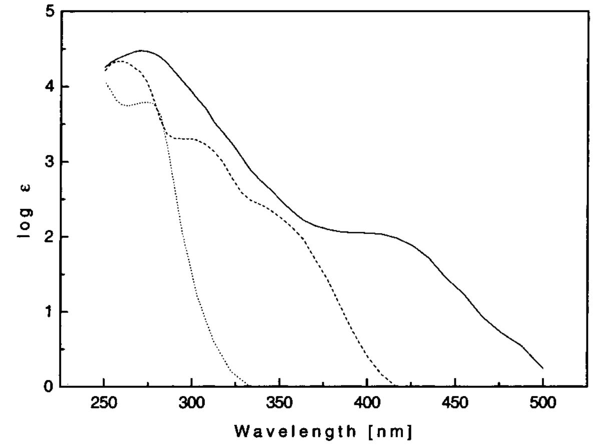
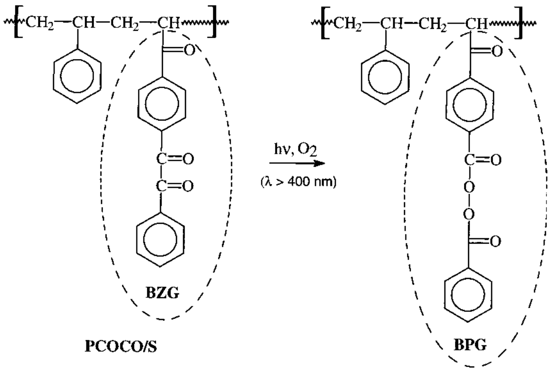


Figure 1. UV/vis absorption spectra in chloroform of (—) poly[1-phenyl-2-(4-propenoylphenyl)-1,2-ethanedione], (- - -) poly[(4-acetylphenyl)vinylketone], and (• • •) BP.

Scheme 2



and irradiated in a "merry-go-round" apparatus at ambient temperature using the filtered output of a 125 W medium-pressure mercury lamp: for 366 nm, a 4 mm Corning 5860 glass filter (USA); for >360 nm, a 4 mm Jenaer 730 glass filter; for >400 nm, a combination of 4 mm Jenaer 730 and 4 mm Jenaer 691 glass filters (Jena, Germany). The distance of the films from the axis of the cylindrical lamp was 8 cm. In experiments in which a greater photon flux at >400 nm was needed, a Spectramat (Ivoclar A. G., Schaan, Liechtenstein) apparatus (350−530 nm) was used in combination with a UV CL SR HPR plastic film filter (LLumar, USA). Thermal decompositions of photochemically formed peroxides in films were conducted in air at 91 ± 1 °C in the column oven of a Shimadzu gas chromatograph.

IR spectra were recorded on a NICOLET 400 (Nicolet, Germany) FT spectrophotometer.

Results and Discussion

Photochemical Generation of Benzoyl Peroxide Carbonyl Groups (BPG) in PCOCO/S Copolymer Films. 1,2-Diketones have much lower triplet state energies (E_T) and absorb at significantly longer wavelengths than monoketones. For instance, E_T of benzil is ca. 54 kcal mol^{-1} whereas that of acetophenone (the corresponding monoketone) is ca. 74 kcal mol^{-1};[12] from energy-transfer experiments, E_T of BP can be estimated as ≤59 kcal mol^{-1}.[13] Additionally, BP does not absorb UV radiation above 340 nm in solution.[14] As shown in Figure 1, the benzilcarbonyl groups (BZG) of PCOCO/S extend the red absorption edge well beyond 400 nm.

Therefore, initial irradiations of PCOCO/S were performed at >400 nm to ensure that the primary excited states are from the BZG. At ambient temperature in air, the characteristic IR stretching band of the 1,2-di- and monocarbonyl groups (1660−1690 cm^{-1}) decreased progressively to ca. 50% of their initial intensities after ca. 200 h of irradiation. Further irradiation under these conditions led to small changes in IR spectra of the films. The residual peak belongs to monoketones present in the structure of pendant group of the copolymer, which absorb in the same region as the dicarbonyl groups. Loss of intensity in the 1660−1690 cm^{-1} region was accompanied by growth of new, intense bands in the 1750−1800 cm^{-1} region that are characteristic of a diacyl peroxide (Figure 2).[15] The 1700−1750 cm^{-1} region in the spectra also indicates the presence of small amounts of esters that may arise from the slow thermal or sensitized photochemical[13] decomposition of the BPG photoproducts. Scheme 2 describes the principal process that is occurring.

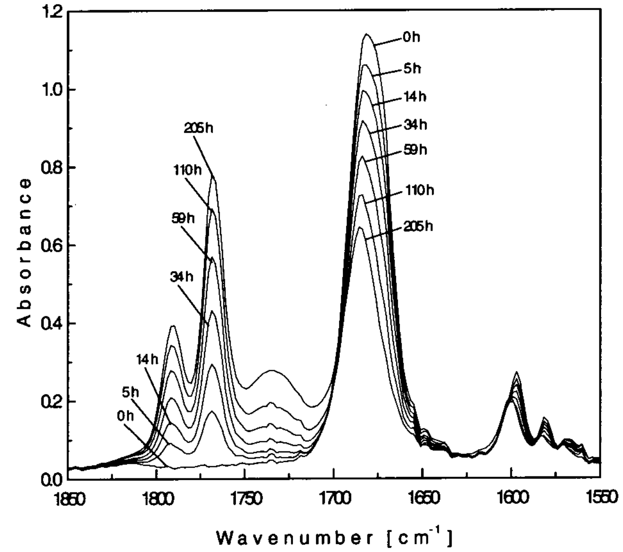


Figure 2. FT-IR spectra of a PCOCO/S copolymer film irradiated at RT in air for various periods at >400 nm.

UV−vis spectra in the region of the diketone n−π^* absorption band (~410 nm) were also recorded during irradiation (λ > 400 nm) of PCOCO/S films in the Spectramat (Figure 3). There is a continuous decrease in absorbance at 410 nm, and only the tail of a stronger band is detectable after 3 h of irradiation.

Irradiations of PCOCO/S films at ambient temperature in air, using >360 nm radiation (2% transmittance at 366 nm), also led to formation of BPG (Figure 4), but with much more ester than is formed with >400 nm radiation. The esters are produced probably by both singlet[16] and triplet[17] photosensitized decomposition (monocarbonyl sensitizers) of peroxy groups in BPG after their initial formation. The rate of formation of BPG is faster than their rate of destruction during the first 7 h; thereafter, the relative rates become inverted (Figure 5). Initially, radiation is absorbed preferably by diketone groups, and the presence of molecular oxygen allows efficient formation of peroxides. The importance of photodecomposition of the peroxy groups increases as the fraction of radiation absorbed by the arylcarbonyl part of the BPG increases, and consequently, the rate of additional peroxide formation decreases. The BP alone do not absorb at >330 nm (Figure 1), but alkyl(aryl)ketones from BPG (for example, poly[(4-acetylphenyl)vinylketone] in Figure 1) do. The combination of both chromophores in BPG should absorb, also. Therefore, BP is decomposed at longer wavelengths in

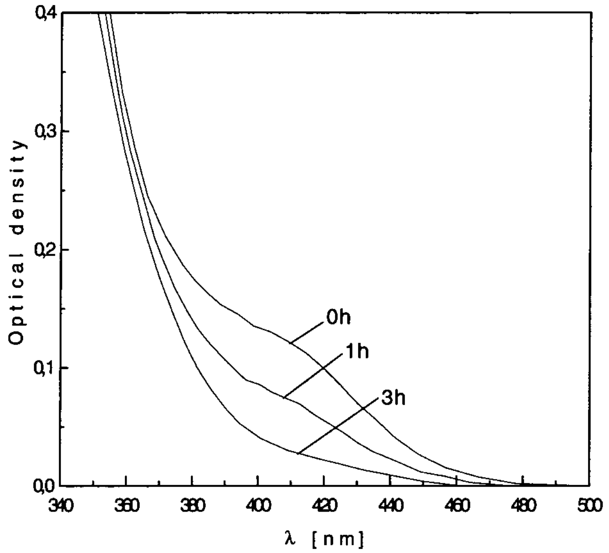


Figure 3. UV–vis absorption spectra of a PCOCO/S film as a function of irradiation time in a Spectramat apparatus (>400 nm) at RT in air.

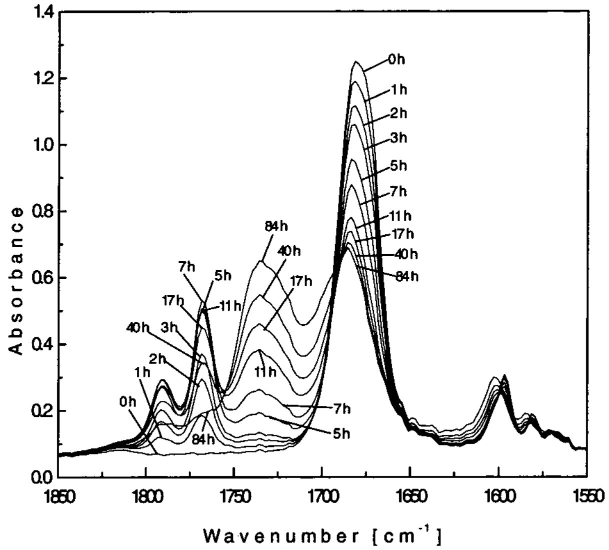


Figure 4. FT-IR spectra of a PCOCO/S copolymer film irradiated at RT in air for various periods at >360 nm.

BPG than it is alone, and a part of the decomposition is sensitized.

Figure 6 indicates the formation of only small amounts of BPG at all stages of irradiation of films at 366 nm; the maximum IR absorbance at 1750–1800 cm^{-1} occurred after 6 h. We assume that transformation of BZG to BPG (Scheme 2) is still the principal reaction pathway, but photodecomposition of the peroxides is very rapid. Alternatively, excitation of 1,2-diketo groups of BZG at 366 nm may lead to different reaction pathways (as observed at >400 nm) that do not involve formation of BPG. However, no significant dependence on the distribution of photoproducts from BZ itself on irradiation wavelengths >300 nm in solution was observed.[16] Regardless, Figure 6 demonstrates that the detected BPG do not survive irradiation at 366 nm (vide infra). As mentioned above, the fraction of radiation absorbed by the keto groups of BPG increases as the conversion of BZG moieties to BPG progresses.

Photosensitized Decompositon of Photochemically Generated BPG in PCOCO/S Films. The loss of BPG, generated by prior irradiation of BZG within PCOCO/S at >400 nm, can be induced by irradiation at 366 nm. The results have been followed by IR spectral changes, as before (Figure 7). Even with the effect of the additional conjugation afforded by the para carbonyl substituent, the excited states of para carbonyl in BPG (>70 kcal mol^{-1}) are sufficiently energetic to cleave –O–O– bonds ($E_D \sim 33$ kcal mol^{-1}).[18] This system may be thought of as an intrachromophoric sensitization, similar to the photodecomposition of polymeric peroxy esters investigated previously by Neckers and co-workers.[19–21] A possible mechanism (Scheme 3) involves conversion of potential energy of the excited states to kinetic energy for homolytic bond cleavage. The Norrish type I cleavage reaction of ketones is a more common example of this process.

Decreases of peroxide IR absorbances (1750–1800 cm^{-1}) in Figure 7 are accompanied by large increases in absorbances from ester groups (1700–1750 cm^{-1}) and very slight increases near 1690 cm^{-1}, where benzoic acids (known thermal decomposition product of BP[16]) absorb.

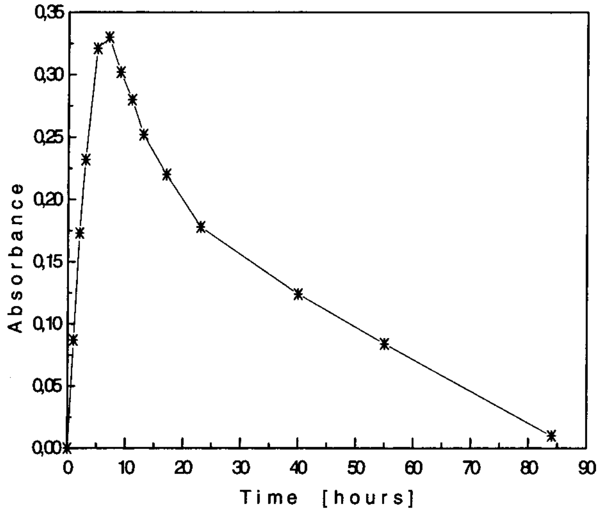


Figure 5. IR absorbance changes at 1769 cm^{-1} (from Figure 4) in a PCOCO/S film vs time of irradiation (λ > 360 nm) at RT in air.

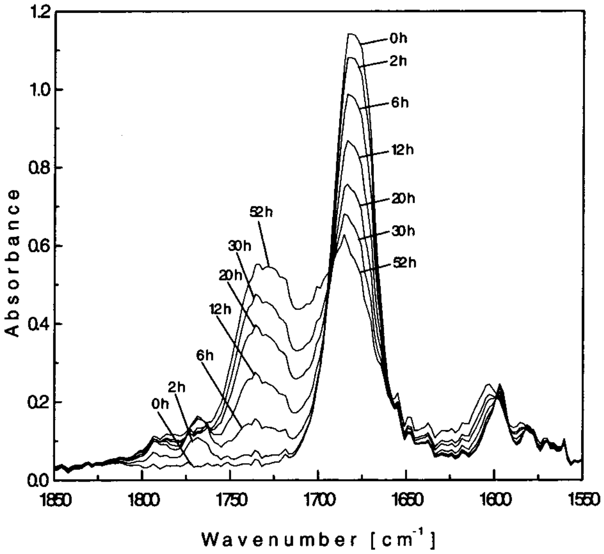


Figure 6. FT-IR spectra of a PCOCO/S copolymer film irradiated at RT in air for various periods at 366 nm.

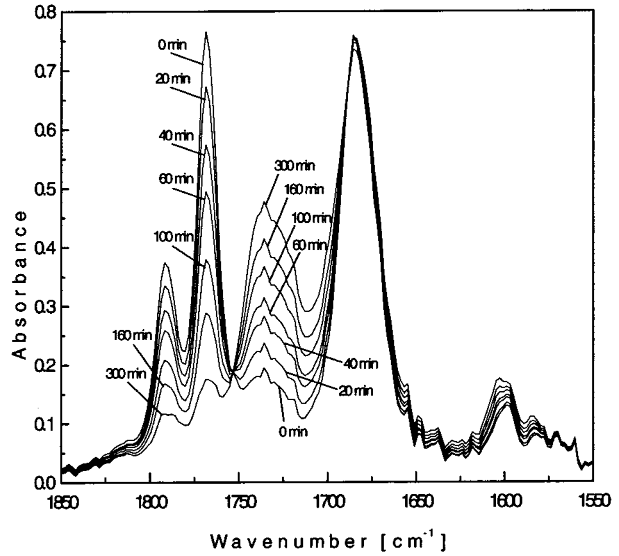
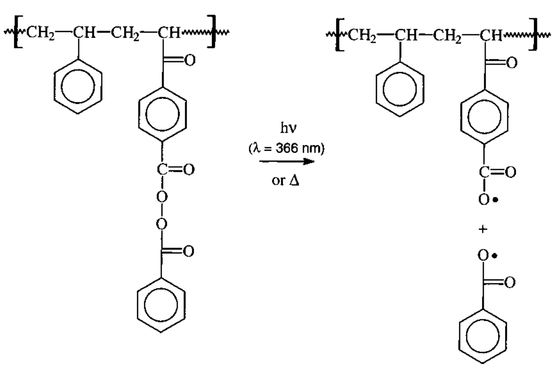


Figure 7. FT-IR spectra of a BPG-containing copolymer (formed by prior irradiation of a BZG in a PCOCO/S copolymer film at >400 nm at RT in air) upon irradiation at 366 nm at RT in air; see text for details.

Scheme 3



For comparison purposes, PS films containing 10 wt % BP molecules and 10 wt % poly[4-acetylphenyl(vinyl)-ketone] as a triplet sensitizer (i.e., in concentrations comparable to the chromophoric contents of BPG formed in the PCOCO/S copolymer) have been irradiated at 366 nm (Figure 8). Even after 285 h of irradiation, only a small fraction of the BP was lost. These results are very different from those found using irradiated PCOCO/S films that contain preformed BPG. They indicate that the efficiency of energy transfer from excited states of the polymeric chromophores in poly[4-acetylphenyl-(vinyl)ketone] (that are congregated within a relatively small volume fraction of the PS matrix) to BP molecules is inefficient. In addition, the lack of complete compatibility of PS and poly[4-acetylphenyl(vinyl)ketone] allows formation of discrete ketone-rich domains. Regardless, this experiment indicates that the BP molecules do not absorb a significant fraction of the incident 366 nm radiation and do not undergo direct photochemical decomposition in the presence of the other strongly absorbing species.

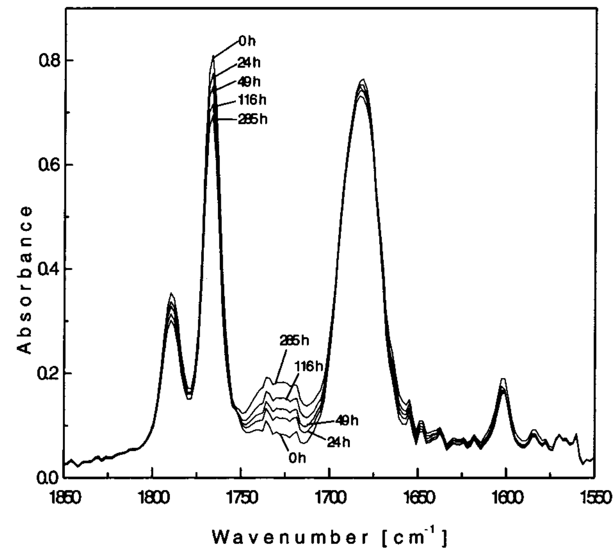


Figure 8. FT-IR spectra of 10 wt % BP and 10 wt % poly[(4-acetylphenyl)vinylketone] in a PS film irradiated at RT in air at 366 nm.

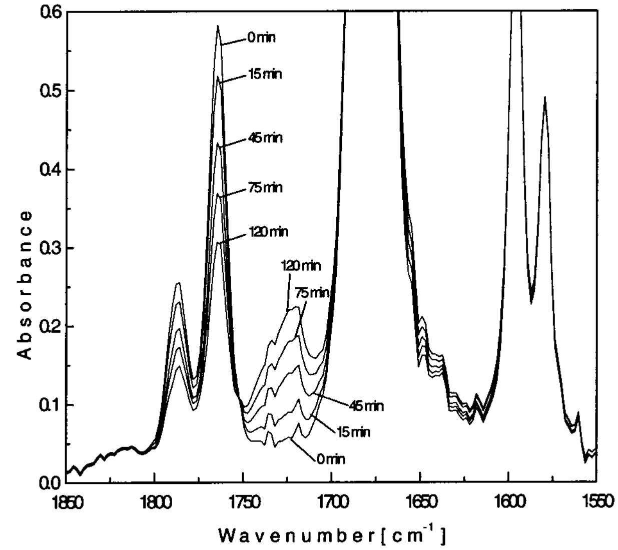
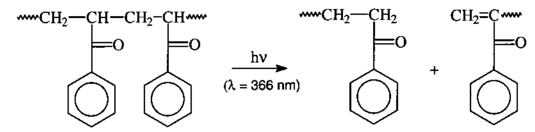


Figure 9. FT-IR spectra of 10 wt % BP in a poly[phenyl-(vinyl)ketone] film irradiated at RT in air at 366 nm.

Scheme 4



When 10 wt % BP was doped into a neat poly[phenyl-(vinyl)ketone] homopolymer film, to increase the ease of contact energy transfer, the relative rate of photochemical decomposition was comparable to that of BPG in copolymer films, but significant degradation of the polymer matrix was evident even at early stages of reaction (Figure 9). We suspect that besides Norrish II cleavages along the chains of poly[phenyl(vinyl)ketone] (Scheme 4), radicals from BP decomposition also contribute to main-chain scissions of the polymer; it is much less probable that radicals from the (noncovalently attached) BP than those from the BPG can lead to cross-linking.

Thermal Decomposition of Photochemically Generated BPG in PCOCO/S Films at 91 °C. To compare the results from photochemically induced (366 nm) transformation of BPG (Figure 7), the course of the thermal reactions at 91 °C was also examined by IR spectroscopy (Figure 10). After 32 h, the peaks from peroxide at 1750−1800 cm^{-1} were reduced almost to baseline levels. Progressive decreases in peroxide absorbances were accompanied by increases of IR absor-

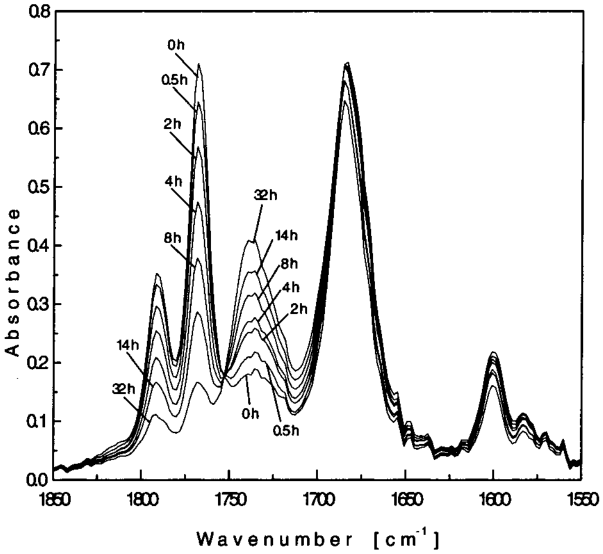


Figure 10. FT-IR spectra of BPG-containing copolymer (formed by prior irradiation of BZG in a PCOCO/S copolymer film previously irradiated at RT in air at >400 nm) upon thermolysis at 91 °C in air.

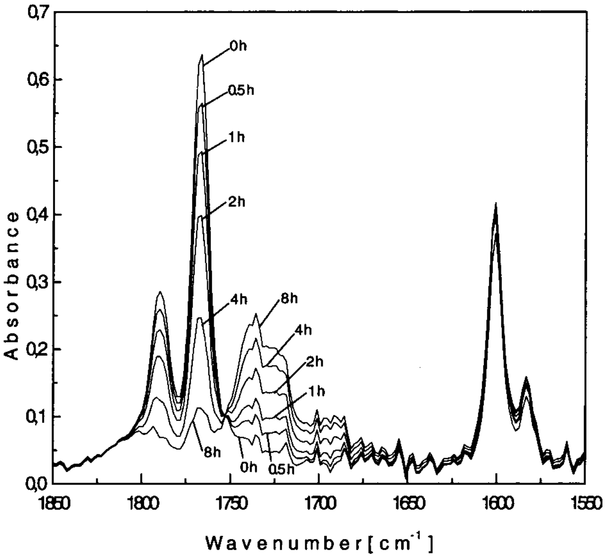


Figure 11. FT-IR spectra of 10 wt % BP in PS film upon thermolysis at 91 °C in air.

bance bands attributed to ester groups (1700−1750 cm^{-1}), and the overall changes are very similar to those induced photochemically. However, comparisons of Figures 7 and 10 indicate that the amount of benzoic acids (1670−1700 cm^{-1}) was somewhat higher during the thermal decomposition than the photochemical one (in analogy with results from BP in benzene[16]).

The first-order rate constant (k) for loss of BPG groups at 91 °C, 0.077 h^{-1}, was calculated from IR peak intensity changes at 1750−1800 cm^{-1}. As noted qualitatively from the nearly complete disappearance of peroxide peaks after 8 h at 91 °C (Figure 11), 10 wt % BP molecules in PS films react more rapidly than BPG in copolymer films. The rate constant of the former, 0.245 h^{-1}, is about 3 times faster than the latter.

Our literature search indicates that diacyl peroxide groups bound to polymers have been prepared only by photochemical means,[7] and their mechanism of thermal decomposition (as well as rates of decomposition) differs from the same groups in low molecular weight species.[7] In that regard, we have examined the relationship between host structure and the rates of BP decomposition for the systems reported to date. Table 1 lists the rate constants for decomposition of several low molecular weight BP derivatives in PS and BP structures as pendant groups in copolymer matrices at 91 °C. There is a clear trend[7] that electron-withdrawing groups at the 4-position on one ring of BP slow peroxide loss and electron-donating ones enhance it, independent of whether the BP moieties are pendant groups (i.e., covalently linked) or doped into a polymer matrix. This conclusion was made taking into account higher decomposition rate of low molecular peroxides in comparison with polymeric one in consequence of induced decomposition.[7]

Polymer Chain Cross-Linking vs Scission during Photochemical Formation and Decomposition of Peroxides. Prior to irradiation, PCOCO/S films can be dissolved completely in organic solvents like benzene or chloroform at room temperature. After irradiation at >400 nm for 90 h, only 20% of the polymer could be dissolved, and irradiation at >400 nm followed by either irradiation at 366 nm or heating at 91 °C resulted in completely insoluble polymer films.

Since irradiation at >400 nm results almost quantitative loss of BZG (Figure 2), some of the incident radiation may cause cross-linking either as part of the transformation of the BZG or independent of it. As was shown earlier[9] for 1,2-diketo/aroyl bichromophores, photoreactivity is localized predominantly at the species with the lower triplet energy, the 1,2-diketo groups, even when excitation is into the absorption bands of the aroyl part. Our results indicate that irradiations at 366 nm lead predominantly to sensitized decomposition of polymeric peroxides (that initiate polymer chain cross-linking) rather than Norrish type II reactions (that imply main-chain scission). However, after transformation of the BZG and decomposition of the BPG, the subsequent photoprocesses probably involve Norrish type II reactions of the remaining carbonyl groups (photodegradation proceeds)! Assuming that photocross-linking and photodegradation proceed with equal efficiency, the resulting product will be cross-linked (as experimentally found). Reason is, that statistically, only $^1/_4$ of cross-linked structure is split from the cross-link of two macromolecules.

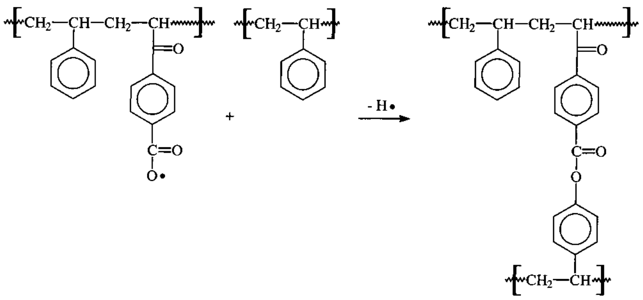
Radicals from thermal or photochemical cleavage of BPG can abstract hydrogen atoms from polymer chains of PS (especially at the benzylic position) or add to a

Table 1. Rate Constants (k) for Thermal Decomposition of BP and BP Derivatives in Polymer Films at 91 °C

BP source and carrier	k (h^{-1})
irradiated PCOCO/S copolymer	0.077
irradiated 1-{4-(2-methacroylethoxy)phenyl}-2-phenyl-1,2-ethanedione/styrene copolymer	0.256[a]
irradiated 1-{4-(2-methacroylethoxy)phenyl}-2-phenyl-1,2-ethanedione in PS	0.43[a]
irradiated 1-{4-(2-acetyloxyethoxy)phenyl}-2-phenyl-1,2-ethanedione in PS	0.40[a]
BP in PS	0.245

[a] Reference 7.

Scheme 5



phenyl ring[22,23] to effect cross-linking (Scheme 5). In addition, other hydrogen-abstraction processes by an electronically excited benzil species or by an acyloxy radical formed in the presence of molecular oxygen[24] can lead to some cross-linking. The polymer-based radicals that are formed[25] have several options for further reaction: combination with another polymeric radical or an acyloxy radical, disproportionation, fragmentation, or rearrangement. Thermal decomposition of BP in PS is known to decrease the molecular weight of the polymer.[23] This indicates that fragmentation of the benzylic-based polymeric radicals (leading to a shortened benzylic radical and a truncated terminal alkene[26]) is more efficient than (bimolecular) two macro radicals combination, leading to a σ bond between two polymer chains. Our solubility studies indicate that cross-linking of PCOCO/S chains during photochemical generation of the BPG and their photochemical or thermal decomposition is preferred to main-chain scission.

Cross-linking may occur by more than one pathway: (1) addition of one acyloxy macroradical to a phenyl ring on another chain (leading to ester formation as shown in Scheme 5); (2) random combinations of two macroradicals whose centers are localized at pendant groups or main-chain benzylic sites (formed, for instance, when a benzoyloxy radical abstracts an H atom from a vicinal polymer chain to yield benzoic acid), as long as they are on different chains. Because of entropic factors, we believe that combinations between primary pendant acyloxy radicals and secondary aryl (from decarboxylation of initial pendant benzoyloxy groups) or alkyl (from loss of a main-chain benzylic H atom, for instance) radicals are less likely than the direct addition of an acyloxy radical to a phenyl ring shown in Scheme 5.[22,23] This hypothesis is also consistent with the observation that polymer-based acyloxy radicals lead mainly to cross-linking while acyloxy radicals generated from noncovalently attached dopant precursors result primarily in chain degradation.

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