Photochemical Transformation of Benzil Pendant Groups of Polystyrene Copolymers into Benzoyl Peroxide Moieties and Their Subsequent Thermal Decomposition. Cross-Linking or Chain Scission?

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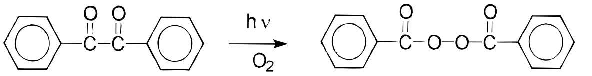
ABSTRACT: Films of the copolymer, 11 wt % 1-{4-(2-methacroyloxyethoxyphenyl}-2-phenyl-1,2-ethanedione (BZMA) and styrene (S) (BZMA/S), as well as polystyrene (PS) doped with either the BZMA monomer (BZMA-PS) or 1-{4-(2-acetyloxyethoxy-phenyl}-2-phenyl-1,2-ethanedione (BZAc-PS) in concentrations that match the composition of the copolymer, have been irradiated ($\lambda > 400$ nm) in the presence of molecular oxygen at ambient temperatures. The rates of consumption of BZMA and BZAc and the concurrent formation of the corresponding benzoyl peroxide-containing units (BPMA and BPAc) were followed by infrared spectroscopy. The rates of benzil-group consumption and peroxide formation matched each other and were virtually the same in the three film types. Larger concentrations of oxygen increased the rate of consumption of BZMA. From a kinetic treatment of data at two concentrations of oxygen in PS, it is concluded that BZMA photooxidation is more than 10 times faster than that of benzil. At 91 °C, the first-order rate constants for thermal decomposition of BPMA and BPAc in PS are equal to and are larger than in the BPMA/S copolymer. The lower rate constant of BPMA/S, as well as the worse fit of the rate data from BPMA and BPAc in PS to a unimolecular decomposition model, is ascribed to some bimolecular decomposition, probably from aggregated peroxides. There is no indication of a bimolecular decomposition component in the copolymer. A very large portion (91 wt %) of BPMA/S, from irradiation of BZMA/S, is THF insoluble (i.e., cross-linked). The insoluble part increases to about 99 wt % after the BPMA/S film is treated at 91 °C for 6 h. Both of the corresponding doped polymers remain completely soluble in THF after irradiation and thermolysis. Cross-linking during the irradiation and heating is ascribed to formation of ester linkages (through abstraction of H atoms from $-O-CH_2-CH_2-O-$ groups by acyloxy radicals) and combination of pendant acyloxy radicals with radical sites on neighboring chains; abstraction from benzylic carbon atoms along PS chains leads to scission. By contrast, irradiation and subsequent heating of BZMA-PS or BZAc-PS films results in more chain scissions than cross-linking since the average molecular weights are decreased.

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]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Recently, we reported that BZ could be converted almost quantitatively to benzoyl peroxide (BP) upon irradiation (>400 nm, i.e., the long wavelength edge of the n → π* absorption band) in aerated polystyrene (PS), poly(methyl methacrylate) (PMMA), and three other polymer matrices (eq 1).[2,3] Here, we examine this reaction in a copolymer film of 11/89 (w/w) 1-{4-(2-methacroyloxyethoxyphenyl}-2-phenyl-1,2-ethanedione/styrene (BZMA/S) (eq 2 in Scheme 1) and in PS doped with equal compositions of BZMA or 1-{4-(2-acetyloxyethoxyphenyl}-2-phenyl-1,2-ethanedione (BZAc) (BZMA-PS and BZAc-PS, respectively). The structures of BZMA and BZAc and the corresponding peroxides are shown in Scheme 2.

Peroxide decompositions in solid polymeric matrices have been investigated as a means to generate primary radicals for cross-linking, grafting, selective degradation, bleaching, polymerization of residual monomers, etc.[4] Polymers with covalently attached BP groups do not appear to have been reported. We have prepared one and compare the changes that occur when it is first irradiated and then heated with analogous results from PS doped with (noncovalently linked) BZMA and BZAc molecules. The preparation and properties of the BZMA monomer and BZMA/S have been described elsewhere.[5]

Experimental Part

Materials. BZMA, BZAc, and a BZMA/S copolymer (M_w = 308 000, M_n = 145 000; containing 11 wt % BZMA) were prepared as described previously.[5] Polystyrene (Vestyron N, Hüls, Germany), poly(methyl methacrylate) (Chemické Závody, Žilina, Slovak Republic), and chloroform (analytical grade) were used as received.

Irradiations and Measurements. Films consisting of 40 mg of BZMA/S (10 cm^2 area) or an equal concentration mixture of BZMA or BZAc in PS were prepared and irradiated ($\lambda >$ 400 nm) in a merry-go-round or a SPECTRAMAT (Ivoclar A. G., Schaan, Liechtenstein) apparatus at ambient temperatures, as described.[2,3]

The thermal decomposition of photochemically formed peroxides in films was conducted in air at 91 ± 1 °C in the column oven of a Shimadzu gas chromatograph. Films were removed periodically for IR measurements.

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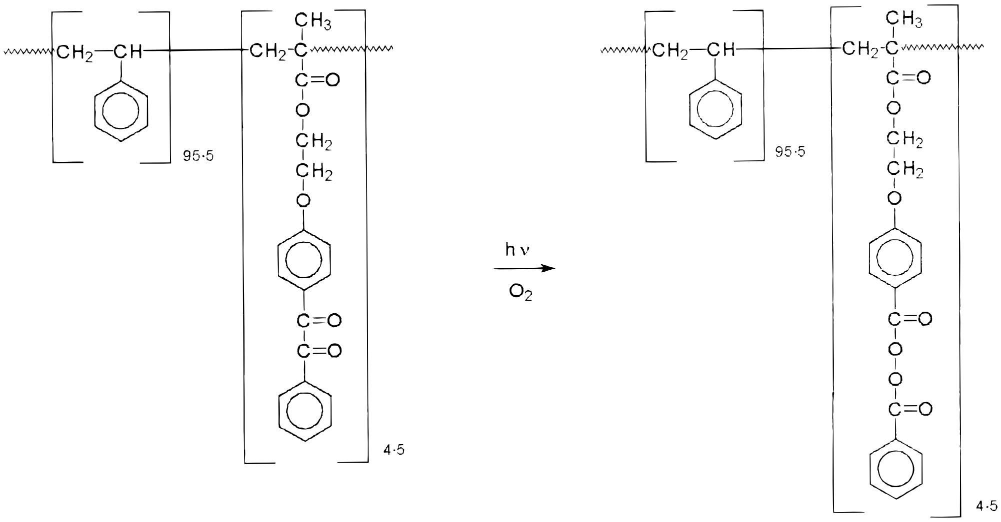
Scheme 1



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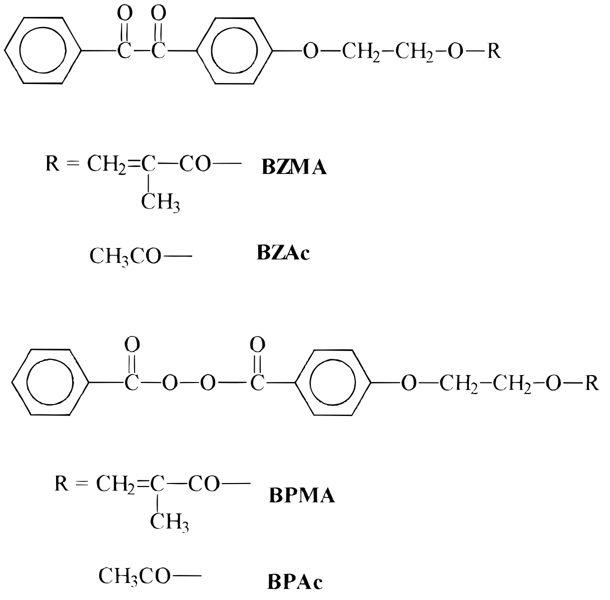
Scheme 2



UV/vis absorption spectra were measured on a SPECORD M40 (Carl Zeiss, Jena, Germany) spectrophotometer. IR spectra were recorded on a NICOLET 400 (Nicolet, Germany) FT spectrophotometer. Molecular weights were estimated by gel permeation chromatography (GPC) with THF (HPLC grade) as eluent, a PSS SDV 5 μm column (d = 8 mm, l = 300 mm), a Waters 515 pump, and a Waters refractive index detector. PS samples of known M_w were used for calibration.

Results and Discussion

Photochemical Formation of Benzoyl Peroxide Pendant Groups in BZMA/S Copolymer Films. As with BZ,[2] BZMA can be photooxidized to a diacylperoxide in PMMA (Figure 1). Peroxide formation from the 1,2-dicarbonyl group is indicated in UV/vis spectra by an isosbestic point at ca. 280 nm and a hypsochromic shift of the $\pi \rightarrow \pi^*$ absorption maximum. Similar UV/vis spectra of PS films with benzil groups cannot be recorded due to the strong absorbance of the phenyl rings of the polymer.

Progress of the irradiations in PS was monitored by infrared spectroscopy, using primarily the decrease in absorbance of the 1,2-dicarbonyl band at 1650−1700 cm^{-1} and the increase in the benzoyl peroxide absorbance at 1750−1800 cm^{-1}. Initially, photoperoxidations of BZMA/S films were compared with those of BZMA monomer and BZAc doped in polystyrene films (Figures 2−4). In Figure 2, the original carbonyl absorbance is reduced to 8% of its original value after 28 h of irradiation. The shift in the absorption maximum to 1686 cm^{-1} may be due to formation of a small amount of benzoic acid in addition to the preponderant product, BPMA.

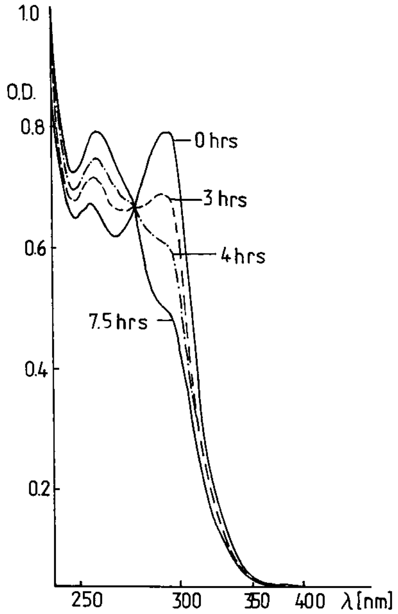


Figure 1. UV spectra of 0.14 mg of BZMA in 20 mg of PMMA (film) upon irradiation in air.

The mechanism for photooxidation of BZMA groups, free or covalently bound to their polymer hosts, is similar to that of BZ. It can be expressed by eqs 3−8.[3] Reaction proceeds from ^{3}BZMA, the excited triplet state of BZMA.[6] Besides photooxidation, quenching of ^{3}BZMA by ground-state oxygen ($^3O_2$) is also possible. Radiationless deactivation of ^{3}BZMA is probably much more important than phosphorescence or reaction with the polymer matrix under our reaction conditions.

$$\mathrm{BZMA} \xrightarrow{h\nu(I_{\mathrm{abs}})} {}^1\mathrm{BZMA} \xrightarrow{\Phi_{\mathrm{isc}}} {}^3\mathrm{BZMA} \qquad (3)$$

$$ {}^3\mathrm{BZMA} + {}^3\mathrm{O}_2 \xrightarrow{k_{\mathrm{ox}}} \mathrm{BPMA} \qquad (4)$$

$$ {}^3\mathrm{BZMA} + {}^3\mathrm{O}_2 \xrightarrow{k_{\mathrm{q}}} \mathrm{BZMA} + {}^1\mathrm{O}_2(+{}^3\mathrm{O}_2) \qquad (5)$$

$$ {}^3\mathrm{BZMA} \xrightarrow{k_{\mathrm{d}}} \mathrm{BZMA} + \Delta \qquad (6)$$

$$ {}^3\mathrm{BZMA} \xrightarrow{k_{\mathrm{ph}}} \mathrm{BZMA} + h\nu \qquad (7)$$

$$ {}^3\mathrm{BZMA} + \mathrm{polymer} \xrightarrow{k_{\mathrm{P}}} \mathrm{reduction\ products} \qquad (8)$$

Assuming steady-state conditions and constant oxygen concentrations, and given the low intensity of incident radiation and low optical densities employed, eq 9 can be derived.[3]

$$\ln \frac{[\mathrm{BZMA}_0]}{[\mathrm{BZMA}]} = \frac{k_{\mathrm{ox}} 2.303 \epsilon_{\mathrm{BZMA}} l I_0 \Phi_{\mathrm{isc}} [{}^3\mathrm{O}_2] t}{(k_{\mathrm{ox}} + k_{\mathrm{q}})[{}^3\mathrm{O}_2] + k_{\mathrm{d}} + k_{\mathrm{ph}} + k_{\mathrm{P}}} = kt \qquad (9)$$

$[\mathrm{BZMA}_0]$, $[\mathrm{BZMA}]$, ϵ_{BZMA}, l, and I_0 are the concentrations of BZMA at irradiation times = 0 and t, the decadic molar extinction coefficient of BZMA at the wavelengths of irradiation, the thickness of the film, and the intensity of the incident light, respectively.

If transformation of BZMA to BPMA is quantitative, eq 10 describes the formation of BPMA with time.

$$[\mathrm{BPMA}] = [\mathrm{BZMA}_0](1 - \mathrm{e}^{-kt}) \qquad (10)$$

Equations 9 and 10 can be expressed in terms of BZMA and BPMA absorbances as shown in eqs 11 and 12. Analogous equations apply to the loss of BZAc and the formation of BPAc.

$$A_{\mathrm{BZMA}} = A_{\mathrm{BZMA0}} \mathrm{e}^{-kt} \qquad (11)$$

$$A_{\mathrm{BPMA}} = A_{\mathrm{BZMA0}}(\epsilon_{\mathrm{BPMA}}/\epsilon_{\mathrm{BZMA}})(1 - \mathrm{e}^{-kt}) \qquad (12)$$

Figure 5 presents a plot of the decrease of BZMA absorbance and increase of BPMA absorbance versus irradiation time for a BZMA/S film. The experimental points can be fitted well to eqs 11 and 12. The relative rate constants for parallel experiments are collected in Table 1.

Films were irradiated simultaneously in a merry-go-round apparatus to ensure they received the same radiation doses. The calculated values of k for 1,2-dicarbonyl consumption in films with covalently linked and unbound (i.e., doped) BZMA and unbound BZAc are equal (or nearly so) within the limits of experimental error. Thus, the double bond of BZMA has no influence on the efficiency of peroxide formation. The results also demonstrate that the probable partial aggregation[3] of BZMA or BZAc in PS influences neither the rate of reaction nor the concentration of oxygen accessible to the reactive groups.

The smallest error limits of the rate constants for the 1,2-dicarbonyl consumption (given in Table 1) were calculated in using first six points from Figures 2−4. However, the error limits of the rate constants for peroxide formation, using only the first six points, are significantly higher than those for 1,2-dicarbonyl consumption. When the data set is expanded to include all of the data points in Figures 2−4, the error limits for peroxide formation can be reduced significantly (Table 1).

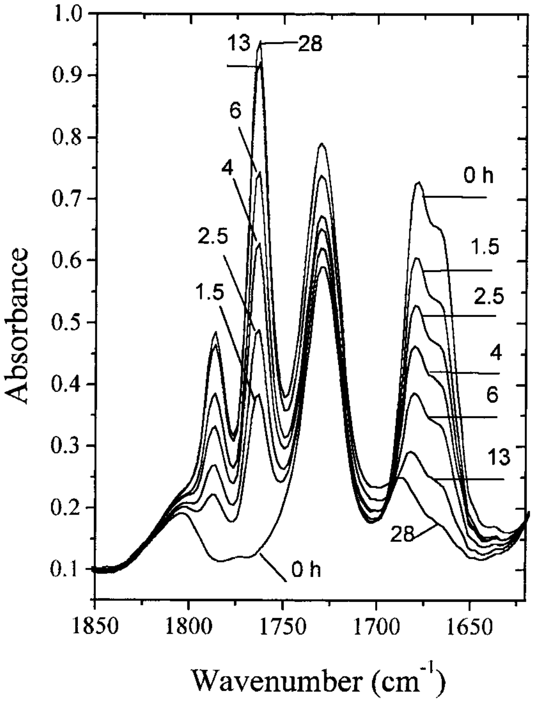


Figure 2. FT-IR spectra of a BZMA/S film irradiated for different periods in air.

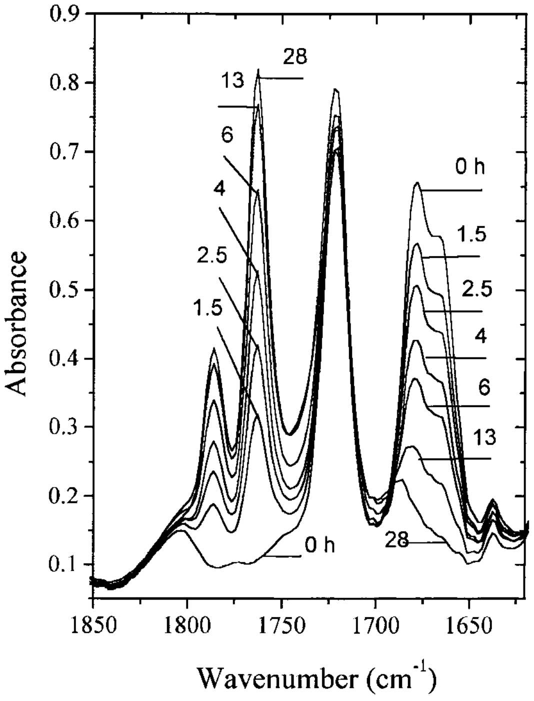


Figure 3. FT-IR spectra of a BZMA-PS film irradiated for different periods in air.

To estimate the dependence of photooxidation of BZMA groups in the copolymer on oxygen concentration, films were irradiated simultaneously in air and in pure molecular oxygen atmospheres in a SPECTRAMAT apparatus. Plots of ln $[A_{\mathrm{BZMA0}}/A_{\mathrm{BZMA}}]$ versus time at

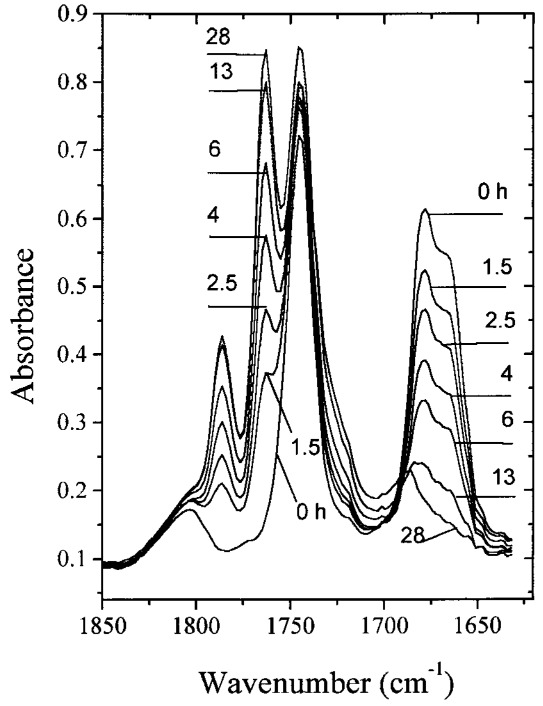


Figure 4. FT-IR spectra of a BZAc-PS film irradiated for different periods in air.

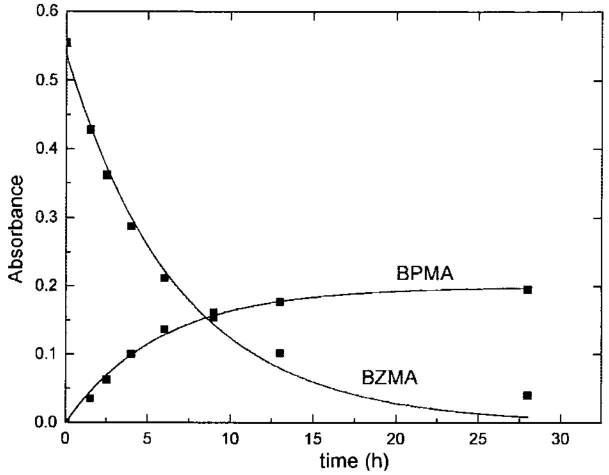


Figure 5. Plot of the decrease of BZMA 1,2-dicarbonyl absorbance (1684 cm^{-1}) and increase of BPMA peroxide absorbance (1784 cm^{-1}) during irradiation of BZMA/S (see Figure 2 for data). Theoretical lines of best fit are drawn through the experimental points.

ambient temperature (Figure 6) are linear. As expected, increasing the oxygen concentration leads to more rapid consumption of BZMA groups. Reducing the temperature to ca. 0 °C decreases the rate of BZMA photooxidation in an oxygen atmosphere was observed (results not included). As temperature is lowered, the equilibrium concentration of oxygen in a film decreases,[7] and the probability that a ^{3}BZMA will encounter a molecule of oxygen before returning to its ground state is diminished.

The ratio of the bimolecular oxidation reactions and the unimolecular deactivation processes[3] is given by $(k_{ox} + k_q)[^3O_2]/(k_d + k_{ph} + k_P)$. Using eq 9 for the observed rate constants of consumption of BZMA in BZMA/S in an oxygen atmosphere and in air (Figure 6), and assuming that the solubility of oxygen in the copolymer

Table 1. Relative Rate Constants (h^{-1}) for Benzil Group Consumption and Peroxide Formation upon Irradiations of Films in Air at Ambient Temperature and Rate Constants for Peroxide Decomposition at 91 °C

film	1,2-dicarbonyl consumption	peroxide formation	peroxide decomposition (R^a)
BZMA/S	0.156 ± 0.004	0.166 ± 0.011	0.256 (0.9999)
	0.163 ± 0.003	0.173 ± 0.013	
BZMA-PS	0.147 ± 0.002	0.169 ± 0.007	0.432 (0.997)
	0.151 ± 0.002	0.165 ± 0.007	
BZAc-PS	0.161 ± 0.002	0.186 ± 0.010	0.404 (0.998)
	0.159 ± 0.004	0.190 ± 0.010	

[a] Correlation coefficient.

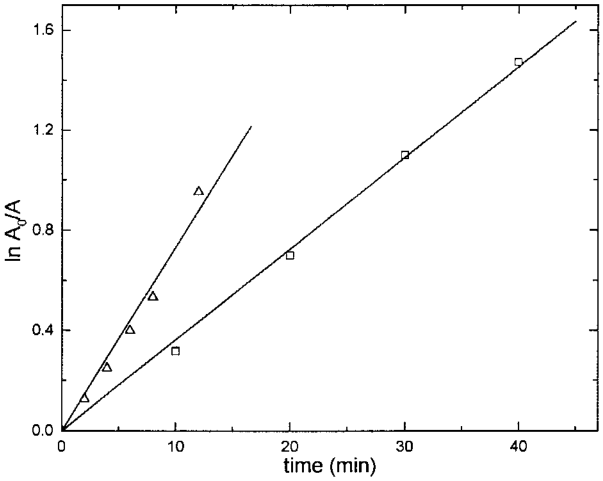


Figure 6. Semilog plots of absorbances at 1684 cm^{-1} for photooxidation of BZMA/S films in air (□) and in oxygen (△) atmospheres.

is the same as that in pure PS ($[^3O_2]_{air} = 1.64 \times 10^{-3}$ mol/kg; $[^3O_2]_{oxygen} = 7.85 \times 10^{-3}$ mol/kg at 25 °C),[3] the ratio $(k_{ox} + k_q)[^3O_2]_{air}/(k_{ph} + k_d + k_P)$ is calculated to be 0.57. This ratio is more than 1 order of magnitude higher than the corresponding one for BZ consumption in PS.[3] It is doubtful that the unimolecular rate constants are very different for BZ and BZMA triplets. However, the greater electron density in the BZMA chromophore (due to the para alkoxy group on a phenyl ring) may increase $(k_{ox} + k_q)$.

Decomposition of Photochemically Generated Dibenzoyl Peroxides in Polymer Films at 91 °C. The temporal changes that occur when the photooxidized films were treated at 91 °C were followed by IR spectroscopy (Figures 7–9). A decrease of peroxide absorbances (1750–1800 cm^{-1}) was accompanied by an increase of absorbances from ester groups (ca. 1735 cm^{-1}) and benzoic acids (1688 cm^{-1}).

Thermal decomposition of BP in PS is known to yield benzoic acid and small amounts of phenyl benzoate as the low molecular weight products.[8,9] The major portion of the esters is probably attached covalently to phenyl rings of PS.[9] Decompositions of BPMA-PS, BPMA/S, BPAc-PS, and BP in PS[8,9] proceed in very similar fashions. However, absorbance from decomposition products during peroxide decompositions is more pronounced in BPMA-PS, BPAc-PS, and BPMA/S films (Figures 7–9) than in BP-PS films (results not included).[2,3] The greater absorbance from decomposition products of BPMA and BPAc (doped or attached to PS) than BP in PS is an indication that the 1,2-dioxyethane groups (–O–CH$_2$–CH$_2$–O–) of the former afford a new and efficient source of H atoms for abstraction by benzoyloxy

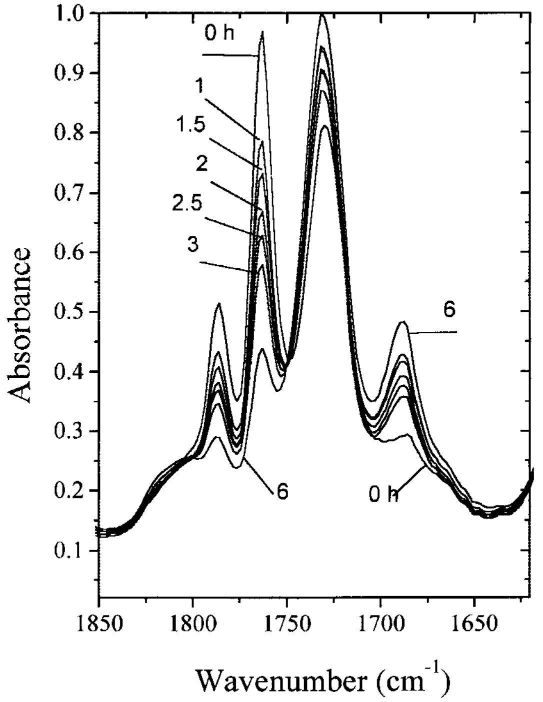


Figure 7. FT-IR spectra of a BPMA/S film heated for various periods at 91 °C. Peroxides were formed by photooxidation of a BZMA/S film (Figure 2).

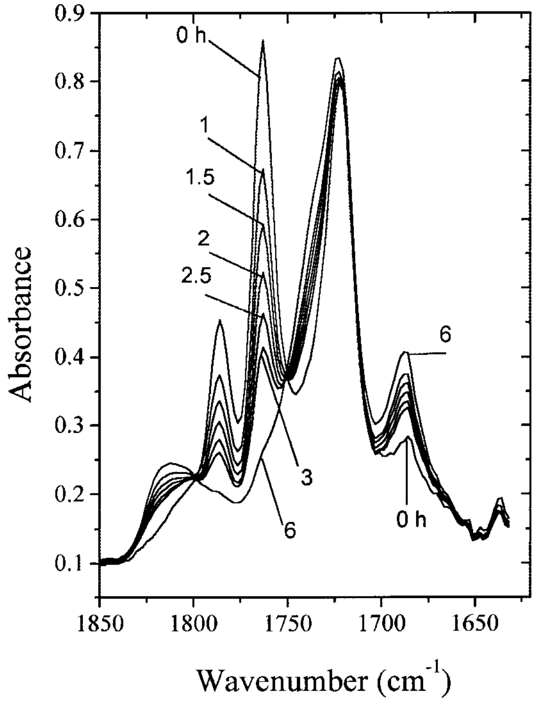


Figure 8. FT-IR spectra of a BPMA-PS film heated for various periods at 91 °C. Peroxides were formed by photooxidation of a BZMA-PS film (Figure 3).

radicals. The homolytic C—H bond dissociation energy of C—H in a benzylic group is somewhat lower than that of a secondary C—H in a 1,2-dioxyethane group.[14] However, entropic (proximity) factors may favor abstraction by benzoyloxy from a nearby dioxyethane group. Some of the differences in product absorptions is due also to physical factors; unsubstituted benzoic acid sublimed under conditions employed to effect BP decomposition. In the case of decomposition of BPMA/S, BPMA-PS, and BPAc-PS, statistically one-half of the carboxylic acids should remain bound to the copolymer or to the moiety containing the larger substituent at the para position of the aromatic ring. In the case of BP-PS, only unsubstituted benzoic acid can be formed. As a result, less benzoic acid than the amount produced was detected in IR spectra of heated BP-PS, BPMA/S, BPMA-PS, and BPAc-PS films; losses were largest for BP-PS.

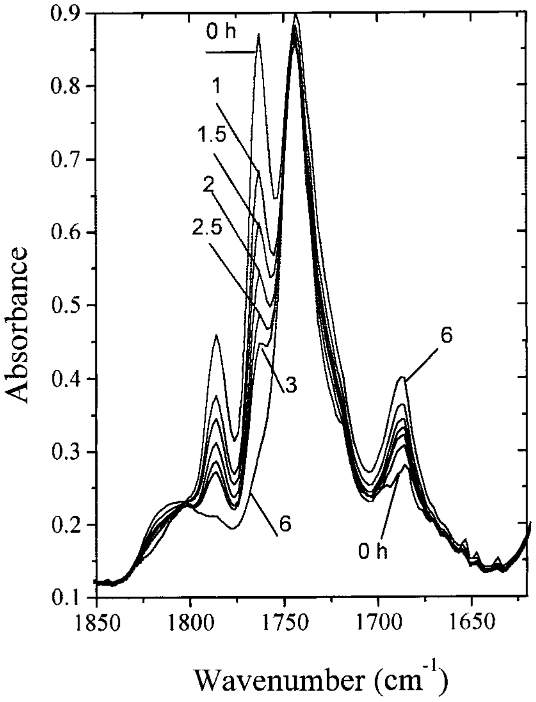


Figure 9. FT-IR spectra of a BPAc-PS film heated for various periods at 91 °C. Peroxides were formed by photooxidation of a BZAc-PS film (Figure 4).

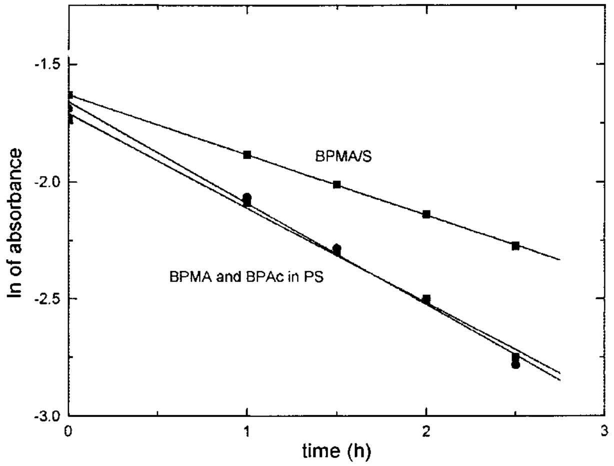


Figure 10. Semilog plots for the thermolysis of BPMA/S, BPMA-PS, and BPAc-PS films at 91 °C. Absorbances are at 1787 cm^{-1} (Figures 7–9).

Semilog plots[10] of the intensity changes in the well-defined peroxide band at 1787 cm^{-1} from Figures 7–9 are presented in Figure 10. The first-order rate constants from linear fits to the data points are collected in Table 1. Decomposition rates are higher, and linear fits are somewhat worse for BPMA-PS and BPAc-PS films than for BPMA/S. Bimolecular pathways (inductive decomposition) also contribute to the thermal decomposition of dopant peroxides in polymer matrices.[4]

The lack of good fits to a strictly unimolecular model for BPMA-PS and BPAc-PS is probably ascribable to the interaction of some bimolecular decay; it further supports the existence of some aggregation in these films.[3] Covalent attachment of BZMA in BZMA/S must be random, and despite the high loading of BPMA after oxidation, the peroxides remain separated in space. Since the bimolecular pathway does not lead to efficient cross-linking,[4] we expect that thermolysis of peroxide bound to the polymer will result in more cross-linking than in the case of dopant peroxide.

The rates of decomposition of the dopant peroxides are 1.6−1.7 faster than that of the covalently attached ones (Table 1). We noted previously that the rate of consumption of benzilic groups (and formation of peroxide groups) are virtually the same in the three films. Apparently, covalent attachment has little influence on the photophysical properties of the benzilic moieties and on the ability of $^3O_2$ molecules to reach them, but it does affect the environment in which the peroxide groups reside. An alternative explanation of the faster decomposition of the dopant peroxides than that of the covalently attached ones beside fast inductive decomposition of the low molecular weight peroxide is that the covalently attached peroxides exist in sites that permit a greater degree of benzoyloxy radical-pair recombination. At 91 °C in a perchlorinated nonviscous solvent, the rates of decarboxylation of a benzoyloxy[11] and a 4-methoxybenzoyloxy radical[12] (a model for the other radical from BPMA) are calculated to be 3×10^7 and 6.5×10^6 s^{-1}, respectively. If there is no H abstraction from the surrounding matrix or cage escape, the radical pair has ample time to recombine. The low molecular weight BPMA and BPAc must reside in similar sites, and their small structural differences have little effect on the decomposition rates. However, *both* pieces of these cleaved peroxides can escape from their cage.

Molecular Weight Changes of Polymer Matrices during Photochemical Formation and Thermal Decomposition of Peroxides. In addition to abstracting a hydrogen atom from a polymer chain of PS (especially from the benzylic position) or from $-O-CH_2-CH_2-O-$ groups of BPMA/S, BPMA-PS, and BPAc-PS, a benzoyloxy radical can add to a phenyl ring.[6,9] In addition, other hydrogen-abstraction processes by an electronically excited benzilic species or by an acyloxy radical formed in the presence of molecular oxygen[15] can lead to cross-linking during the irradiation of the benzil-containing groups. The polymer-based radicals that are formed[10] may combine with another polymeric radical or an acyloxy radical, disproportionate, fragment, or rearrange. In some polymers,[13] such as polyethylene and poly(ethylene oxide), combination of two in-chain radicals leads to cross-linking and an increase of the average molecular weight. Disproportionation between two polymeric radicals results in formation of a saturated structure in one chain and introduction of a double bound in the other, but it does not change the average molecular weight. Thermal decomposition of peroxides in PS is known to decrease the molecular weight of the polymer.[9] This indicates that fragmentation of the benzylic-based polymeric radicals (leading to a shortened benzylic radical and a truncated terminal alkene[13]) is more efficient than (bimolecular) radical combination, leading to a σ bond between two polymer chains.

Table 2. Molecular Weight Changes of Polymer Matrices during Photochemical Formation and Thermal Decomposition of Peroxides

film and treatment	M_n (10^{-5})	M_w (10^{-5})	M_w/M_n	THF soluble part (%)
BZMA/S	1.54	3.25	2.11	100
after $h\nu$	0.380[a]	0.572[a]	1.50[a]	9
after $h\nu + \Delta$	0.129[a]	0.193[a]	1.49[a]	1
BZMA-PS	1.29	3.02	2.33	100
after $h\nu$	1.03	2.53	2.45	100
after $h\nu + \Delta$	0.772	2.60	3.37	100
BZAc−PS	1.24	2.95	2.37	100
after $h\nu$	1.00	2.49	2.48	100
after $h\nu + \Delta$	0.751	1.97	2.63	100

[a] Soluble part.

After irradiation of BZMA or BZAc in PS and subsequent heating at 91 °C, all of the sample remained soluble in THF, and the effective molecular weight of the polymer decreased somewhat (Table 2). The fraction of chains suffering scission, F_s, can be calculated as $F_s = M_{n0}/M_n - 1$, where M_{n0} and M_n are average number molecular weights before and after irradiation and/or irradiation and heating. After irradiation of BZMA-PS or BZAc-PS, $F_s = 0.245 \pm 0.005$; after irradiation and thermolysis, $F_s = 0.66 \pm 0.01$. Since the magnitudes of F_s are independent of the benzilic structure for BZMA and BZAc, the reactivites of the BZ triplet states (and of the acyloxy radicals derived from them) with the PS matrices must be very similar. This conclusion is consistent with our observations that the rates of oxidation of BZMA and BZAc, as well as the rates of thermal decomposition of BPMA and BPAc, are virtually the same.

After BPMA-PS decomposition, a small shoulder was observed in the high molecular weight region of the GPC peak; the net change in M_W was very small (Table 2). In this case, a significant portion of the methacrylic structures leads to radical cross-linking, also. One acyloxy radical (of a geminate pair), formed from BPMA and BPAc in PS, can produce a polymeric radical and benzoic acid (or a derivative thereof). This process leaves one acyloxy radical of the pair intact. If it does not (or cannot) escape from its cage, its probable fate is to become attached to the polymer chain at the site of its radical center (i.e., combination). Only when the polymer radical disproportionates more rapidly than it combines with the acyloxy radical or when the acyloxy radical escapes from the radical-bearing cage or decomposes will subsequent processes result in molecular weight increases or decreases of the polymer. The fraction of out-of-cage reaction increases with the reactivity of the matrix.[4] Since PS does not cross-link during the decomposition of peroxides, radicals formed on the backbone must prefer to disproportionate.

On average, there are 47 molecules of BZMA or BZAc per PS chain in the doped films. If all of the BZMA or BZAc are converted to the corresponding BP moieties, and their thermolysis results in one chain scission per molecule, each polymer chain should be cut into 96 pieces. From our GPC analyses and F_s values, less than 0.5% of the BZMA and BZAc (as well as intermediates from them) or BPMA and BPAc eventually leads to main chain scission. This analysis assumes the absence of chain cross-linking, a process which would offset the effect of chain scission on M_n. Regardless, there is little scission. Most probably, hydrogen atom abstraction by acyloxy radicals from $-O-CH_2-CH_2-O-$ groups of dopant molecules is preferred to reaction with benzylic centers of PS chains (despite the relative energetics for the two processes[14]). A second possibility is that hydrogen abstraction from benzylic sites along the polymer backbone is mostly by the more reactive, unsubstituted benzoyloxy radical,[11] leaving the less reactive 4-alkoxybenzoyloxy radical[12] to *combine* with the polymer. The higher IR absorption of thermal decomposition products (esters and benzoic acid) from BPMA-PS and BPAc-PS compared with those from BP in PS (results not included) is consistent with either of these explanations. Also, decomposition of the acyloxy radicals, which depends on the hydrogen donor ability of the polymer matrix, can lead to less reactive radicals, influencing the effectiveness of chain degradation. Other processes that diminish H abstraction from a PS chain (such as acyloxy radical additions to phenyl rings or reactions with molecular oxygen[6]) should occur at about equal rates in all of the PS system; they cannot explain the results above.

After irradiation of a BZMA/S copolymer film as described above, 91 wt % of the material was insoluble in THF at ambient temperature, presumably due to cross-linking. The gel content increased to 99 wt % after the irradiated film was heated at 91 °C. The effective molecular weights of the native copolymer and the THF soluble portions after irradiation and subsequent heating are presented in Table 2. They indicate that the vast majority of BPMA/S chains are cross-linked in the copolymer even after irradiation without heating. Small fractions of chains have suffered scissions. Clearly, cross-linking dominates scission in the copolymer.

During epoxidation of olefins by thermal decomposition of BP (photooxidation mediated by benzil), Sawaki[15] assumed the presence of acyloxy radicals, also. Their hypothesis allows us to explain how a common intermediate, an acyloxy radical, can participate in both cross-linking and chain degradation during both photochemical formation and thermal decomposition of peroxides. Equal amounts of main-chain scission in the photooxidation step and in thermal decomposition of the peroxide constitute indirect evidence for the presence of acyloxy radicals. However, a mechainism involving abstraction of a hydrogen atom by the excited triplet state of a benzilic structure, and recombination of the radical formed cannot be excluded.

A simple mechanism, in which one unsubstituted *or* para-substituted benzoyloxy radical (of each thermally generated geminate pair from *noncovalently* attached BPMA or BPAc) abstracts a hydrogen atom from a polymer, leads to the prediction that one-half of the benzoyloxy groups will be attached to C-macroradicals and the other half will be transformed into carboxylic acids. Since one side of a peroxide group in BPMA/S is *already* attached to a polymer chain, its scission and reaction as described above predict that *one-half* of the benzoyloxy groups will cross-link chains on a purely statistical basis! Of course, side reactions can diminish the degree of cross-linking. In addition, the actual reactions of a radical pair do not follow the statistical model. Since a benzoyloxy radical is more reactive than a *p*-alkoxybenzoyloxy radical, *more than half of the radical pairs from BPMA/S should lead to cross-linking* in the absence of side reactions. Only combination of a C-macroradical and a *p*-alkoxy-substituted benzoyloxy radical of BPMA/S can lead to a cross-link. Regardless, thermolysis of BPMA/S is expected to result in extensive cross-linking.

Circumstantial support for efficient cross-linking upon thermolysis of BPMA/S films comes from more detailed analyses of data in Figure 7. After 6 h at 91 °C, $>75\%$ of the peroxide absorbance at 1786 cm^{-1} is lost. Furthermore, this analysis indicates that the ratio of the relative yields of the acid and ester products is about 0.5. However, we cannot exclude some thermooxidation of the polymer as contributing to the increase in “ester” absorption.

Cross-linking of the BZMA copolymer is initiated by the acyloxy radical pair. In this case, if the (unsubstituted) benzoyloxy radical that is not attached to a polymer chain abstracts an H atom from a *neighboring* BZMA/PS chain, vicinal chains with radical centers will be created. The aforementioned higher reactivity of the unsubstituted benzoyloxy[11] and its higher mobility make this scenario both feasible and preferable. The captive (i.e., chain attached) 4-alkoxybenzoyloxy radical nearby will be both spatially and energetically[12] more disposed to combine with the radical site on the neighboring polymer chain than abstract a hydrogen atom. The resultant ester constitutes the cross-link. The ca. 1:1 acid:ester product ratio from thermolysis of the BPMA/S film (Figure 7) is predicted by this cross-linking scheme.

Other radical combination processes probably occur in competition with cross-linking of the copolymer. For instance, radicals formed on $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$ groups do not lead to main-chain scission. They can either degrade the pendant group or recombine with other acyloxy radicals; M_n may be increased, but it is not decreased. Benzoate (absorbing at 1735 cm^{-1}; Figure 7) is probably formed upon combination of both free and polymer-attached acyloxy radicals with radical centers derived from $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$ groups. Also, combination of a *free* benzoyloxy radical with a polymeric radical of any kind does not make a discernible change in the molecular weight distribution since the molecular weight of the starting copolymer is high. As a corollary, a small amount of cross-linking causes large changes in the molecular weight distribution. The results presented clearly demonstrate that cross-linking is favored over degradation in the copolymer.

A major conclusion arising from this work is that BZ-type groups can cross-link *or* degrade polymeric chains. The process that dominates is dependent upon the kind of polymer and how the BZ groups are placed within a polymer matrix.

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