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Synthesis, photoperoxidation and crosslinking of styrene copolymer with pendant benzil moieties

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Abstract

A new benzil-containing (BZ) styrene monomer, 1-phenyl-2-{4-[2-(4-vinylbenzyloxy)ethoxy]phenyl}-ethane-1,2-dione (BZS) and its copolymer with styrene (BZS/S) were prepared. BZS concentration in the monomer mixtures is almost identical to the concentration in the copolymers and therefore the chemically homogeneous styrene copolymers are produced. When irradiated ($\lambda = 436$ nm) in the air, the pendant BZ groups of the BZS/S copolymer are transformed into benzoyl peroxide (BP) groups. The BP groups can be converted to esters and benzoic acid moieties during subsequent thermal treatment, resulting in highly crosslinked films.

Keywords: Benzil; Crosslinking of polystyrene; Photoperoxidation

1. Introduction

Methods of polystyrene (PS) crosslinking using a small amount of copolymerized crosslinker are scarce. According to our knowledge, vinyl benzocyclobutene structure incorporated into PS chains was used for its crosslinking [1,2]. Crosslinking of these materials proceeds at a temperature exceeding 200 °C via a coupling reaction of two benzocyclobutene structures, which was exploited for the preparation of architecturally defined nanoparticles via intramolecular chain collapse [1]. A generalized approach for the applications of these materials to the modification of solid surfaces, such as a wide variety of metal, metal oxide, semiconductors, and polymeric surfaces is described [2]. Also in a chloroform solution the formation of crosslink between PS chains with phenylindene pendant groups via their photo-dimerization was studied [3].

Polymers bearing BZ units in the main chain or as pendant groups have been examined as potential negative [4] or positive [5] resist materials based on photo degradation of their polymer networks. They were exploited as water-soluble polymeric photoinitiators [6]. Also, thermoporometry with carbon tetrachloride as a liquid probe has been used to study the crosslinking of polymers bearing BZ units [7]. Finally, the photochemical properties of copolymers bearing BZ pendant groups have been investigated in solution [8].

BZ is an industrially important member of the class of molecules with 1,2-dicarbonyl functionality. The solution-phase photochemistry of BZ has been investigated extensively, both in the presence and absence of molecular oxygen. BZ is photostable in absence of molecular oxygen without hydrogen donor. 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) [9]. However, in aerated glassy polymer films upon irradiation at $\lambda > 400$ nm (i.e., the long wavelength edge of the $n \rightarrow \pi^*$ absorption band, where BP does not absorb), BZ can be converted almost quantitatively to BP [10,11]. Covalently attached BP pendant groups have also been formed by irradiation of copolymer films containing BZ structures [12–14].

Whereas a decomposition of low molecular peroxides doped into PS film results in a net decrease in polymer molecular weight [12,15], the decomposition of pendant BP groups in copolymers is an efficient method of polymer crosslinking [12–14] (Scheme 1). Complete crosslinking of copolymers with pendant BZ groups was also achieved in only one step by irradiation at a shorter wavelength (366, 313 or 254 nm) [13,14]. At a shorter wavelength, the incident light simultaneously decomposes the

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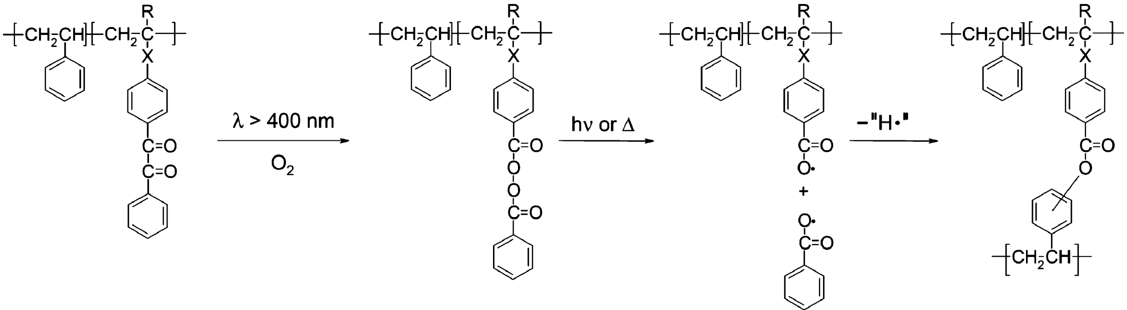
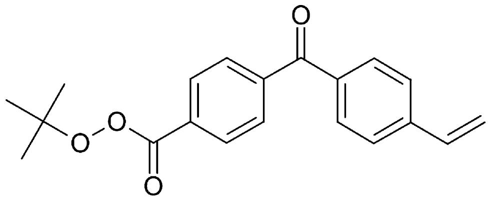


a) X = CO-O-CH$_2$-CH$_2$-O; R = CH$_3$ [12]
b) X = CO; R = H [13]
c) X = chemical bond; R = H [14]
d) X = 4-C$_6$H$_4$-CH$_2$-O-CH$_2$-CH$_2$-O; R = H (BzS/S - present work)

Scheme 1. Photoperoxidation of copolymers bearing pendant BZ groups followed by thermal or photochemical crosslinking.

formed peroxides. As in the previous cases [12–14], the copolymer of styrene with low percentages of *p*-vinylbenzophenone-*p*′-*tert*-butyl perbenzoate (Scheme 2) has been observed to crosslink efficiently with light [16–18]. While it is possible to presume similar crosslinking efficiency between perester [16] (Scheme 2) and BZ pendant groups [12–14] (Scheme 1), the synthesis of the monomer without potentially explosive perester group (Scheme 2) seems to be more convenient.

It has been found in all studies performed to date [12–14] that monomers bearing BZ structures are more reactive than styrene in free radical initiated copolymerizations. Consequently, the concentration of the monomer units bearing BZ structures was higher in the copolymer than in the monomer mixture (at less than complete conversions of the monomers). To avoid chemical heterogeneity of the formed copolymer, a new monomer with presumed lower reactivity than previous monomers [12–14], 1-phenyl-2-{4-[2-(4-vinylbenzyloxy)ethoxy]phenyl}-ethane-1,2-dione (BZS) and its copolymer with styrene (BZS/S) were prepared. The photoperoxidation of the 1,2-dicarbonyl moieties of the BzS/S copolymer, and the process of BP groups decomposition leading to the efficient crosslinking was studied. The new monomer BZS can overcome the difficulties in the preparation of chemically homogeneous copolymers with styrene, and facilitate preparation of copolymers of equal reproducible quality. Therefore, a more regular network than previously obtained [12–14] can be formed. To minimize the extent of the side reactions during the photoperoxidation step [8–10], the lowest possible energy irradiation wavelength of 436 nm was selected.



Scheme 2. Structural formula of *p*-vinylbenzophenone-*p*′-*tert*-butyl perbenzoate.

2. Experimental

2.1. Materials

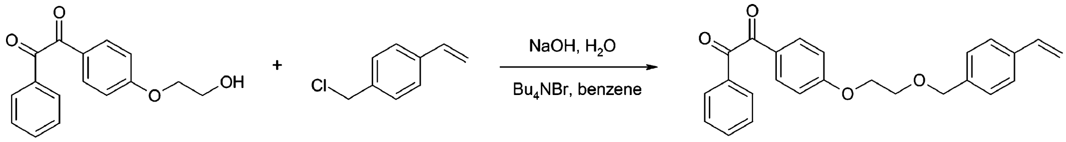
1-[4-(2-Hydroxyethoxy)phenyl]-2-phenylethane-1,2-dione was prepared as reported previously [19,20]. 4-Vinylbenzyl chloride (Aldrich), *tert*-butylammonium bromide (Lachema, Brno, Czech Republic), 2,2′-azobis(2-methylpropionitrile) (AIBN) (Aldrich), tetrahydrofuran (THF, HPLC grade), benzene, chloroform, dichloromethane, ethanol and methanol (analytical grade) were used as received. Stabilized styrene (Aldrich) was washed with diluted sodium hydroxide solution and water, dried with anhydrous MgSO$_4$ and distilled.

2.2. Instrumentation

FTIR spectra were recorded on an Impact 400 spectrophotometer (Nicolet Instrument Corporation, WI, USA). ^{1}H and ^{13}C NMR spectra were measured on a Bruker AM 300 spectrometer (Germany) using chloroform-*d* as a solvent and tetramethylsilane (TMS) as internal standard. UV/vis absorption spectra were measured on a Shimadzu 1650PC spectrophotometer (Japan). Melting points are uncorrected and were measured on a hot stage apparatus. Molecular weights were estimated by gel permeation chromatography (GPC) with THF as a mobile phase, a PSS SDV 5 μm column (d = 8 mm, l = 300 mm), a Waters 515 pump, and a Waters refractive index detector. The instrument was calibrated with PS standards (Polymer Standards Service, Mainz, Germany).

2.3. Monomer synthesis

1-Phenyl-2-{4-[2-(4-vinylbenzyloxy)ethoxy]phenyl}-ethane-1,2-dione (BZS) was prepared according to Scheme 3. Benzene (200 mL), 4-vinylbenzyl chloride (10.7 g, 70 mmol), 1-[4-(2-hydroxyethoxy)phenyl]-2-phenylethane-1,2-dione (10 g, 37 mmol) and Bu$_4$NBr (1.2 g, 3.7 mmol) were added to 20 mL of a stirred aqueous NaOH (7.4 g, 185 mmol) solution. The reaction mixture was stirred for 10 days in the dark at room temperature. The benzene layer was separated, washed with



Scheme 3. Synthesis of BZS.

water, dried with anhydrous $MgSO_4$, filtered, and concentrated. The product was isolated by column chromatography on silica gel with dichloromethane as an eluent to afford 7.4 g (52%) of yellowish powder, mp 128–130 °C.

^{1}H NMR ($CDCl_3$): δ (ppm) = 8.00 − 7.91 (m, 4H, CH–C_{ipso}–CO–CO–C_{ipso}–CH), 7.65 (tt, J = 7.5, 1.5 Hz, 1H, H_{para}), 7.51 (t, J = 7.5 Hz, 2H, H_{meta} from C_6H_5), 7.40 (d, J = 8 Hz, 2H, CH–C_{ipso}–CH=CH_2), 7.31 (d, J = 8 Hz, 2H, OCH_2–C_{ipso}–CH), 7.00 (d, J = 9 Hz, 2H, CH–C_{ipso}–O), 6.71 (dd, J = 17.5, 11 Hz, 1H, CH=CH_2), 5.75 (dd, J = 17.5, 1 Hz, 1H, ArCH=CH_2 (Z)), 5.24 (dd, J = 11, 1Hz, 1H, ArCH=CH_2 (E)), 4.61 (s, 2H, OCH_2Ar), 4.22 (t, J = 4.5 Hz, 2H, ArOCH_2), 3.84 (t, J = 4.5 Hz, 2H, CH_2–CH_2–O–CH_2).

^{13}C NMR ($CDCl_3$): δ (ppm) = 194.8 (C=O), 193.1 (C=O), 164.2 (C_{ipso}–O), 137.3 (C_{ipso}), 137.2 (C_{ipso}), 136.5 (CH=CH_2), 134.7 (C_{para}), 133.2 (C_{ipso}), 132.3 (C_{ar}), 129.9 (C_{ar}), 128.9 (C_{ar}), 128.0 (C_{ar}), 126.3 (C_{ar}), 126.3 (C_{ipso}), 114.9 (C_{ar}), 114.0 (CH=CH_2), 73.2 (CH_2), 68.0 (CH_2), 67.9 (CH_2).

IR (KBr): 1677 (C=O), 1659 (C=O), 1630 (C=C, vinyl), 1601 cm^{-1}.

MS (m/z): 425 (M + K), 409 (M + Na), 242.

UV/vis ($CHCl_3$): λ_{max}[nm] (log ε) = 289 (4.26), 387 (2.05).

2.4. Polymerization

An ampoule containing BZS (0.200 g, 0.517 mmol), styrene (4.545 g, 43.64 mmol) and AIBN (5 mg) was sealed under argon and polymerized at 60 °C for 6.5 h. The copolymer was precipitated three times from chloroform solution into methanol to yield 1.31 g (28%) of slightly yellow copolymer. Residual BZS monomer still present in the copolymer was removed by Soxhlet extraction with ethanol. The content of BZS in the copolymer was determined to be 3.9 wt.% by ^{1}H NMR using the integrated peak areas of separated 3 methylene groups and the aromatic hydrogens of BZS and aromatic styrene hydrogens. GPC: $M_n = 2.1 \times 10^5$ g molL^{-1} and $M_w = 4.0 \times 10^5$ g molL^{-1}.

^{1}H NMR ($CDCl_3$): δ (ppm) = 7.98 (t, 4H-arom. of BZS), 7.64 (t, 1H-arom. of BZS), 7.50 (t, 2H-arom. of BZS), 7.43–6.88 (m, 3H-arom. of S + 6H-arom. of BZS), 6.88–6.29 (m, 2H-arom. of S), 4.54 (br.s, CH_2 of BZS), 4.19 (br.s, CH_2 of BZS), 3.76 (br.s, CH_2 of BZS), 1.85 (br.s, CH of S + CH of BZS), 1.43 (br.s, CH_2 of S + CH_2 of BZS).

^{13}C NMR ($CDCl_3$): δ (ppm) = 164.1 (C_{ipso}-O of BZS), 145.2 (C_{ipso} of S), 134.6 (C_{para} of BZS), 133.1 (C_{ipso} of BZS), 132.3 (C_{ar} of BZS), 129.8 (C_{ar} of BZS), 128.9 (C_{ar} of BZS), 127.9 (C_{ar} of S), 127.5 (C_{ar} of S), 126.1 (C_{ar} of BZS), 125.6 (C_{ar} of S), 114.8 (C_{ar} of BZS), 73.3 (CH_2 of BZS), 67.8 (2 × CH_2 of BZS), 43.8 (CH_2 of S), 40.3 (CH of S). Owing to the low concentration, several peaks corresponding to BZS structure (both C=O and most of C_{ipso}) are not visible in the spectrum.

IR (film): 1678 (C=O).

2.5. Irradiations and measurements

Films of 40 mg of BZS/S copolymer with good optical quality about 40 μm thick, were prepared by casting from 1 mL benzene solutions onto a glass plate (10 cm^2 area). The plate was covered by a Petri dish to slow solvent evaporation. The self-supporting polymer films were separated from the glass by dipping into distilled water. Films were dried to a constant weight at room temperature under vacuum and were irradiated at ambient temperature in air. A homemade "merry-go-round" apparatus was employed. It consisted of a 125 W medium pressure mercury arc placed in a circulating-water-jacketed quartz tube which was surrounded by a 1 cm-thick layer of a liquid filter (500 g NaBr and 3 g $Pb(NO_3)_2$ per 1000 mL aqueous solution) transmitting at $\lambda > 330$ nm. The distance of each sample (placed in rotating 8-rectangular holders) from arc was about 8 cm. Finally, a glass filter Hg Mon 436 (Carl Zeiss, Jena, Germany) transmitting in region 410–510 nm with maximum at $\lambda = 436$ nm (46.5%) was placed in front of each sample. Thermal decomposition of the formed peroxides in the irradiated films was conducted in the air at 91 ± 1 °C in the column oven of a Shimadzu gas chromatograph.

3. Results and discussion

3.1. Synthesis and characterization of the BZS/S copolymer

The contents of BZS in the monomer mixture and in the copolymer are compared with published results from radical copolymerizations of other BZ containing monomers and styrene [12–14] in Table 1. Similarly to BZS/S copolymer in Table 1, a copolymer with higher content of BZS was prepared as well (not included in this work). The content of BZS in the monomer mixture was 13.25 wt.% and in the copolymer it was 12.8 wt.% at 19% conversion. The small difference between the concentrations of the monomer mixtures and in the copolymer at a low conversion enables us to confirm our assumption that the rates of conversion of the two monomers are about equal and that the new BZS/S copolymer exhibits a statistical distribution of BZ pendant groups in its polymer chains. The mutual reactivity of styrene with its 4-substituted derivatives is known to depend on the nature of the substituent [21]; reactivity increases with the decreasing electron donating character of the substituent. The substituent of BZS (4-CH_2OR group) is slightly electron donating. Therefore, BZS should be slightly less reactive than styrene and substantially less reactive than 4-vinyl benzil containing strongly deactivating 1,2-dicarbonyl structures in position 4 (X

Table 1
Content of BZS in the monomer mixture and in its copolymer with styrene as well as data for related copolymers of monomers bearing BZ group and styrene

X[a]	*R*[a]	Conversion (wt.%)	Mol% of BZ monomer		Reference
			In monomer mixture	In copolymer	
CO–O–CH_2–CH_2–O	CH_3	29.5	1.68	3.7	[12]
CO	H	17.9	3.8	11.1	[13]
Chemical bond	H	51.6	2.44	4.9	[14]
4-C_6H_4–CH_2–O–CH_2–CH_2–O	H	27.6	1.17	1.1	Present work

[a] See Scheme 1.

is chemical bond and R = H in Scheme 1) [14]. It is known that the reactivity of methacroyl (X = CO–O–CH_2–CH_2–O and R = CH_3) [12] and of vinyl carbonyl (X = CO and R = H) [13] derivatives is higher than that of styrene in copolymerization with styrene [21]. Our results are consistent with this trend. Therefore, the monomer BZS must be distributed almost statistically in the BZS/S copolymers.

3.2. Photoperoxidation of BZS/S copolymer (Scheme 1)

During the irradiation of the BZS/S copolymer films in air (Fig. 1), the loss of intensity from BZ carbonyl stretching bands at 1650–1690 cm^{-1} and the growth of BP carbonyl stretching bands at 1750–1800 cm^{-1} are clearly seen in FTIR spectra. In the subtracted spectra (Fig. 2), the decrease in aromatic absorption (1597 and 1574 cm^{-1}) is caused by a lower extinction coefficient of the product (BP structures) in comparison with the starting BZ structures. An increase of the absorption at 1607 cm^{-1}, as the result of the product absorption shift, is also seen in the subtracted spectra (Fig. 2). The development of the spectra during irradiation is similar to that of the free BZ in PS [10,11] and BZ pendant groups in copolymer films [12–14]. The advantage of the BZS/S copolymer in comparison with methacrylate and vinyl carbonyl derivatives (case a and b in Scheme 1) is that the copolymer does not contain other groups (e.g. ester or other carbonyl) absorbing in the region of the main changes in IR spectra. Therefore, the monitoring of photoperoxidation and the decomposition of peroxides in BZS/S copolymer by means of IR spectroscopy is much simpler as in previously mentioned copolymers. After the dissolution of the irradiated BZS/S copolymer in chloroform, an insoluble (crosslinked) part was clearly seen in the solution, which was determined to be 23%.

One aim of this research was to prepare peroxide-containing polymers that retain their solubility in organic solvents. As seen in Fig. 1 and better in Fig. 2, it was impossible to avoid the formation of some side products (1700–1750 cm^{-1}) which led to crosslinking even using the mildest possible radiation (436 nm) which is absorbed only by the red edge of the BZ $n \rightarrow \pi^*$ absorption band. Therefore, similarly as it was at $\lambda > 400$ nm [12–14], even at $\lambda = 436$ nm (present work) it is impossible to avoid partial crosslinking in the photoperoxidation step near the complete conversion.

What is the origin of this crosslinking? The main reaction of benzil excited triplet state in the presence of a hydrogen donor in inert atmosphere is hydrogen abstraction under ketyl and alkyl radical formation [22–25]. Benzil excited triplet state cannot abstract aromatic hydrogen [22–26] and formed alkyl radical on the polystyrene backbone prefer to disproportionate (main chain scission), not recombine (crosslinking) [15]. Therefore hydrogen abstraction probably does not participate in the crosslinking.

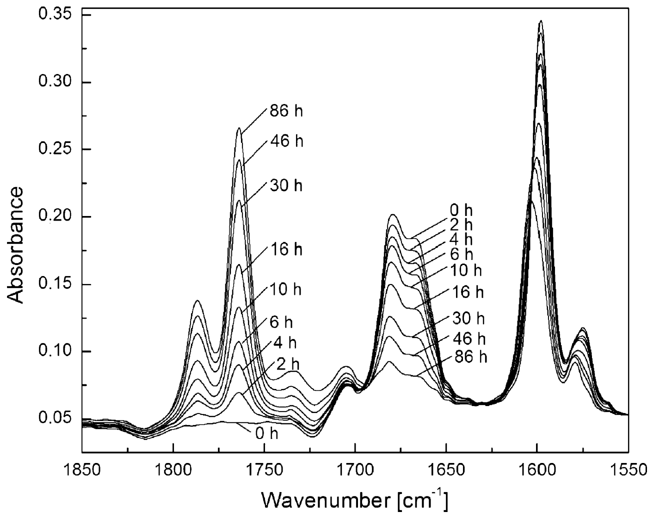


Fig. 1. Changes in FTIR spectra of a BZS/S copolymer film during irradiation ($\lambda = 436$ nm) at room temperature in air. The spectrum of PS was subtracted.

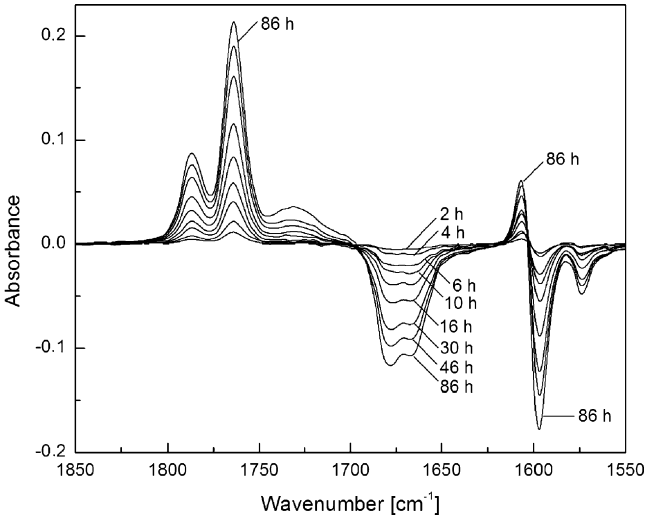


Fig. 2. Changes in FTIR spectra of BZS/S copolymer films irradiated at room temperature in air at $\lambda = 436$ nm. The spectrum of the unirradiated copolymer was subtracted.

During the 103 h of irradiation of free BP in PS film at the same condition, no decomposition of BP was observed. Therefore, the crosslinks are not formed by thermal nor direct photochemical decomposition of BP during irradiation.

Because the majority of the side product is formed at the end of irradiation at the highest BP concentration, the side products are formed probably from labile BP. There is also experimental support for this hypothesis. The side product absorbs in the same region as the decomposition products of BP do (1700–1750 cm^{-1}). At the lowest concentration of BZ the decomposition of BP is most important. Therefore excited BZ (singlet, or triplet) states, at the given conditions, probably do not sensitize the decomposition of BP. This conclusion supports also the sensitized decomposition of BP studies [27,28]. Some new absorbing species as possible sensitizing structures (conjugated double bonds?) present to the end of 436 nm light irradiation in irradiated film (Fig. 4) probably can sensitize decomposition of peroxide structures via efficient singlet energy transfer.

The depletion of the original dicarbonyl concentration in BZS structures (negative values) and the formation of a product (bound BP structures, positive values) are also proven in the changes recorded in Fig. 3. For the free BZ in PS (spectrum not given), a decrease is observed at 1209 cm^{-1} and an increase at 1223 cm^{-1} only. The same changes as for the free unsubstituted BZ are also observed in very similar region during irradiation of BZS/S copolymer film. Therefore, the changes at 1212 cm^{-1} and 1227 cm^{-1} correspond to the bonding of carbonyl to the unsubstituted phenyl ring in BZS structure. In the BZS structure, beside the carbonyl bound to phenyl ring, there is yet another carbonyl bound to the phenyl substituted in position 4 (Scheme 1). The rest of the peaks corresponds to bonds of the initial carbonyl structure of BZS attached to an ethoxy substituted phenyl ring (1165 cm^{-1}) and to carbonyl groups connected to the ethoxy substituted phenyl ring in bound BP structures (1240 cm^{-1}).

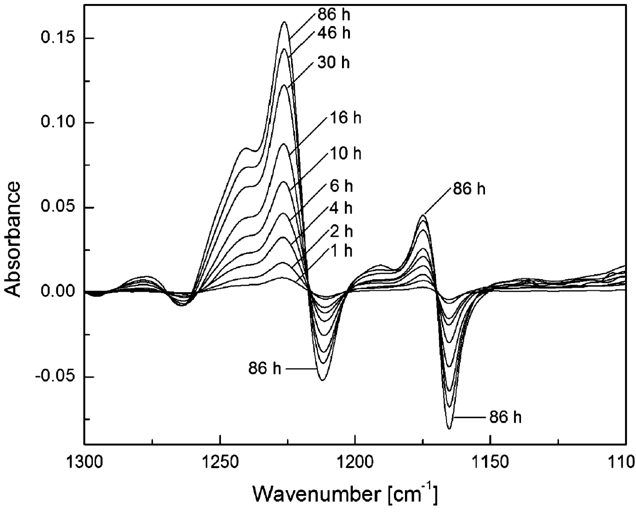


Fig. 3. Changes in FTIR spectra of BZS/S copolymer films irradiated at room temperature in air at λ = 436 nm. The spectrum of the unirradiated copolymer was subtracted.

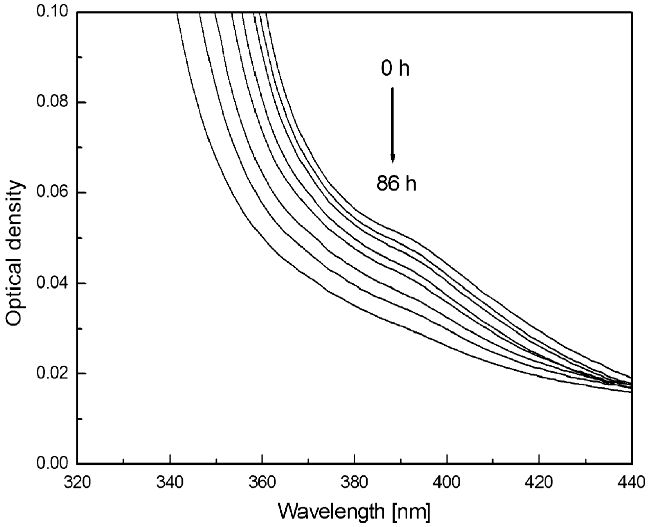


Fig. 4. Changes in UV/vis spectra of BZS/S copolymer films irradiated at room temperature in air at λ = 436 nm.

Also, the decrease of electronic absorption in the regions of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands (Fig. 4) during irradiation can be attributed to the conversion of BZ to BP moieties.

3.3. *Thermal crosslinking of photoperoxidized BZS/S copolymer*

The BP structures in the BZS/S copolymer formed during irradiation in the air were decomposed in a subsequent thermal step at 91 °C. The loss of BP and the formation of new products can be followed easily by means of FTIR spectroscopy (Fig. 5). The decrease of the absorption of carbonyl groups in BP (1750–1800 cm^{-1}) and the formation of aromatic esters structures (stretching band of the carbonyl of the ester groups with absorption maximum at 1735 cm^{-1}) and benzoic acid structures (stretching band of the carbonyl of carboxylic acid groups at 1660–1690 cm^{-1}) can be seen in the FTIR spectra.

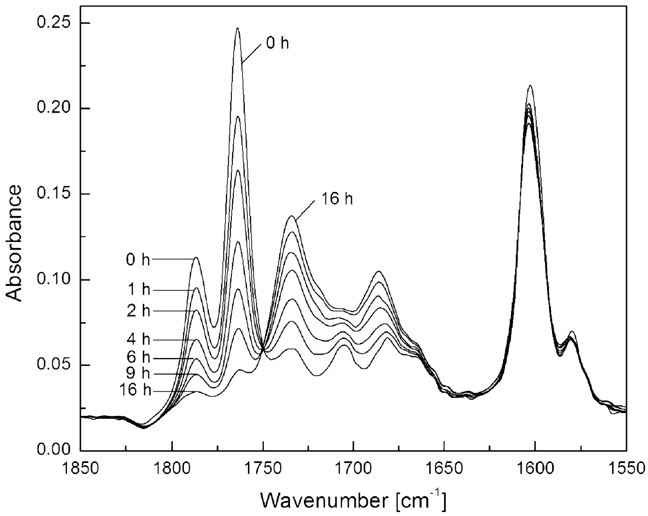


Fig. 5. Evolution of FTIR spectra due to the thermal decomposition of BP groups in a preirradiated BZS/S copolymer at 91 °C. The spectrum of PS was subtracted.

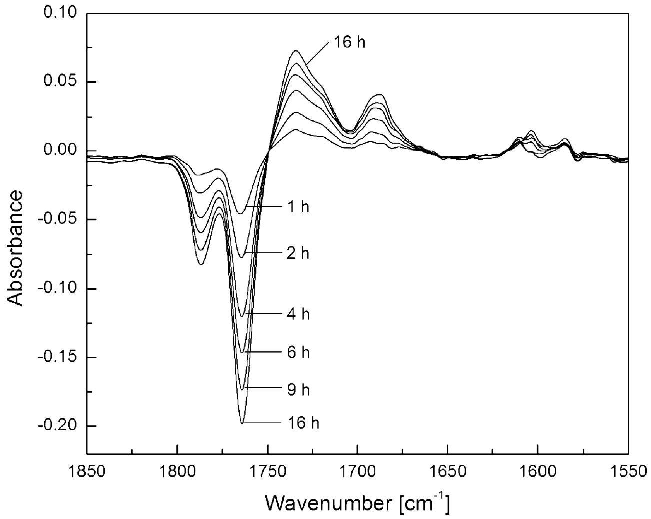


Fig. 6. Evolution of FTIR spectra due to the thermal decomposition of BP groups in a preirradiated BZS/S copolymer at 91 °C. The spectrum of the preirradiated copolymer was subtracted.

The subtracted spectra are more suitable to follow the BP transformations (Fig. 6).

A first-order rate constant for thermal decomposition of BP groups, $k_t = 0.20 \pm 0.01\,h^{-1}$, was calculated (Fig. 7) from IR peak intensity changes at $1763\,cm^{-1}$ (Fig. 5). It is a bit lower than that obtained at the same temperature for the equally 4-substituted BP structure (with the same BZ type photoperoxidized group; $0.26\,h^{-1}$), which was bound to a methacroyl group [12]. Because at a low content of bound BP structures, statistically distributed along the polymer chain in the photoperoxidized BZS/S copolymer, the induced decomposition [29] (chain decomposition – decomposition of BP by the formed radicals) of BP structures can be presumed to be absent or suppressed. At about 4 times higher content of the BP groups (first row in Table 1), not statistically distributed, the contribution of the induced decomposition may be higher as in the later case. Also an evaluation of the BP groups decomposition rate constant by means of IR spectroscopy may be less precise in the presence of methacroyl carbonyl groups absorbing closely to the carbonyl of peroxide.

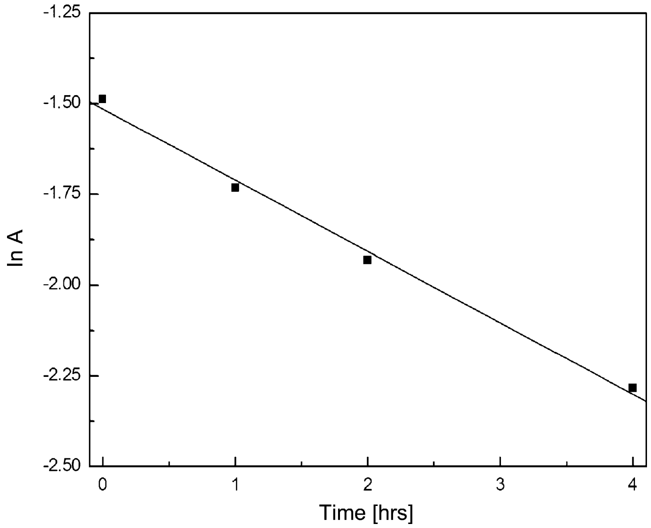


Fig. 7. Semilog plot for the thermolysis of photoperoxidized BZS/S film at 91 °C. Absorbance (A) is at $1763\,cm^{-1}$ (Fig. 5).

After the thermal treatment, the polymer films are completely insoluble in organic solvents due to extensive crosslinking, which is induced by the decomposition of the BP groups. For the BZS/S copolymer as well as for the copolymers described earlier [12–14], a common crosslinking scheme (discussed previously [14]) can be imagined (Scheme 1).

What is the advantage of this method of crosslinking? The PS crosslinking based on the decomposition of a small amount of the covalently bound peroxide or perester group and the subsequent addition of formed polymeric benzoyloxy radical to an aromatic ring of PS seems to be easier and more probable as the known methods of photo-crosslinking based on cycloadditions [18]. The main reason of lower efficiency for cycloadditions is that the reactants at a low concentration present in the copolymer can find their counterpart only with difficulties. In this connection it is interesting to mention the high crosslinking efficiency of surface nano-layers caused by the thermal coupling reaction of two benzocyclobutene structures in PS structure in melt [2]. Some features of the crosslinking of PS according the Scheme 1 are equal to that of the direct methods of the photochemical formation of reactive species, which can react directly with the polymeric substrate under the formation of a network [16,18] (nitrenes, carbenes, excited triplet state of carbonyl compound, or a sensitized decomposition of perester). From these methods only photosensitized decomposition of peresters was sufficiently efficient [16]. At the decomposition of BP and perester structures, the same active species (polymeric benzoyloxy radicals) are formed and their concentrations do not differ much, so it is possible to deduce similar efficiency for both systems. For the modification of surfaces, the method of crosslinking of copolymers with pendant BZ groups based on the access of oxygen in both photoperoxidation and the addition of formed benzoyloxy radical to aromatic ring steps [12–14], seems to be advantageous. An investigation of the influence of variation in chemical heterogeneity of the starting copolymer on the crosslink density of the irradiated and heated films of BZS/S copolymer is in progress.

4. Conclusions

A new monomer BZS, bearing BZ group, has been copolymerized with styrene and has been found to be of comparable reactivity during free-radical polymerization as styrene. As a consequence, the copolymers are much more chemically homogeneous than previously prepared copolymers with styrene in which the other monomers containing a BZ group were used. BZ structural units in films of BZS/S copolymer were converted to BP structures upon irradiation in the air. The use of mild irradiation conditions ($\lambda = 436\,nm$) did not completely stop the formation of species, which led to partial crosslinking during irradiation. Pendant BP structures are thermally unstable, and treatment at 91 °C resulted in significant crosslinking of their copolymers as indicated by the complete insolubility of the films in organic solvents and by IR spectra.

Acknowledgments

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