Crosslinking of polystyrene film by di(4-dibenzoyl peroxide) ether synthesized or formed *in situ* using visible light-induced photo-peroxidation of 4,4'-oxydibenzil

Martin Danko [a], Jaroslav Mosnáček [a,b], Shiao-Wei Kuo [c], Ivan Lukáč [a,*]

[a] *Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava 45, Slovakia*
[b] *Centre for Advanced Materials Application, Slovak Academy of Sciences, Dúbravská cesta 9, 845 11, Bratislava, Slovakia*
[c] *Department of Materials and Optoelectronic Science, Center of Crystal Research, National Sun Yat-Sen University, Kaohsiung, Taiwan*

ARTICLE INFO

ABSTRACT

Upon irradiation ($\lambda > 400$ nm) in aerated glassy polystyrene (PS) film, 4,4'-oxydibenzil (**BZ-O-BZ**), possessing two benzil (BZ) moieties in its structure, undergoes insertion of molecular oxygen between carbonyls of BZ moieties leading to the formation of di(4-benzoyl peroxide)ether (**BP-O-BP**).

In addition, there may be decomposition of the benzoyl peroxide (BP) structures that are photosensitised intramolecularly by BZ structures in **BP-O-BZ** intermediates. Thermal decomposition of the **BP-O-BP** yields two acyloxy radicals, which can either be added to the phenyl rings of PS resulting in crosslinking or in a combination of the liberated hydrogen to form an acid. Acyloxy radicals may also react with the chain of PS causing degradation (main chain scission). The thermal decomposition of the synthesised **BP-O-BPs** and added to high-molecular PS films produces a fully crosslinked material and higher crosslink densities than the peroxides prepared *in situ* by irradiation of **BZ-O-BZ**. The mechanism of the PS crosslinking with the **BP-O-BP** synthetically prepared as well as the **BP-O-BP** prepared *in situ* photochemically is elucidated. PS crosslinking with **BP-O-BP** represents a new and effective method of PS crosslinking.

1. Introduction

The synthesis of crosslinked polystyrene (PS) by copolymerisation of styrene with bi- or multi-functional monomers is a common method for the preparation of crosslinked polystyrene. Since the use of a monomer mixture for the preparation of crosslinked thin PS films for the planar technology would be inconvenient and complicated, a less frequently used post-polymerisation crosslinking of PS is the technique of choice.

For post-polymerisation crosslinking, high-energy radiation methods such as beta, gamma [1–3] or UV—C radiation for relief formation have been used [4]. A self-crosslinkable PS was prepared by the post-modification of PS with reactive groups, *e.g.* maleinimide [5] or iodide [6] or by post-modification of poly(4-chloromethyl styrene) with light-sensitive structures such as benzophenone, stilbazolium, fluorenone, carbazole and sulphonyl azide [7]. Self-crosslinkable PS can also be prepared by copolymerisation of styrene and a monomer containing a reactive functional group, *e.g.* azide [8], peroxo-ester [9,10],

benzocyclobutene [11], phenylindene [12], azide-alkyne [13] or benzil after its photo-peroxidation [14–19].

It has been shown that the visible light irradiation of benzil (BZ) in aerated glassy polymer films leads to photo-peroxidation, and benzoyl peroxide (BP) is formed quantitatively [20–22]. Light of a wavelength of $\lambda > 400$ nm has been used. In this region, due to the presence of carbonyl groups of the diketone, BZ shows the $n \rightarrow \pi^*$ absorption band, while the BP formed does not.

At a later stage, this research was extended to study photo-crosslinkable polymers containing BZ moieties as pendant units [14–19] or as part of the backbone [23,24]. These polymers were shown to have the potential for use as a positive [19] and negative photoresist [16] as well as for surface modification by grafting [25].

The method of the addition of low-molecular weight crosslinking agents to the PS includes the use of difunctional Friedel-Crafts agents [26] and bisazides [27,28]. It is surprising that, despite its simplicity, this method is not in frequent use. Photo-peroxidation of 1,4-bisbenzil

(BZBZ) is one of these methods (Scheme 1) [29]. The mechanism of crosslink formation is based on photochemical transformation of the BZ moieties to the BP structures. In the intermediate (BPBZ), which is formed in the first photochemical transformation stage and composed of both BP and BZ moieties in one conjugated chromophore, the intramolecular sensitisation leads to complete decomposition of the BP structure and ultimately to the formation of two acyloxy radicals. Both can be added to PS, but only the one which carries the BZ structure can, after binding to the polymer and after the subsequent photo-peroxidation of the BZ, contribute to crosslinking in a thermal reaction. The intramolecularly sensitised decomposition of the BP structures in BPBZ is favoured and prevents the formation of bis (dibenzoyl peroxide) (BPBP). In addition to the crosslinking, cleavage of the polymer chains was also observed.

In the present work, the decomposition of di(4-benzoylperoxide) ether (**BP-O-BP**) formed in the course of photo-peroxidation ($\lambda > 400$ nm) of 4,4′-oxydibenzil containing two BZ chromophores linked with an oxygen atom (**BZ-O-BZ**) (Scheme 1) was investigated for the crosslinking of PS. The formation of **BP-O-BP** is more probable than the formation of BPBP. The formation and influence of an intermediate consisting of one photochemically generated BP structure and the un-transformed BZ structure (**BP-O-BZ**) in PS is discussed. The polymer crosslinking based on photochemical **BP-O-BP** formation followed by heat treatment (dual-curing) appears to be advantageous due to its simplicity and safety, and it is also the subject of a patent application [30].

2. Experimental

2.1. Materials

Benzil (BZ) (Lachema, Brno, Czech Republic), 1,4-Bisbenzil (BZBZ) (TCI), benzoyl peroxide (BP) (Merck, Germany) crystallised, m.p. 105−107 °C, 4,4′-oxydibenzil (**BZ-O-BZ**) (OrgaLight, Givors, France) and polystyrene (Vestyron N, Hüls, Germany, **PS$_V$**) of $M_w = 283$ kg mol^{-1}, $M_n = 106$ kg mol^{-1} and Đ = 2.67 were used as received. Polystyrene with a narrow molar mass distribution (**PS$_N$**, $M_w = 148$ kg mol^{-1}, $M_n = 118$ kg mol^{-1} and Đ = 1.25) was prepared previously [29]. A high-molar mass polystyrene (**PS$_H$**) with $M_w = 884.5$ kg mol^{-1}, $M_n = 451.2$ kg mol^{-1} and Đ = 1.96 was prepared by spontaneous polymerisation of a monomer over a long period without use of a radical initiator; the **PS$_H$** was allowed to precipitate three times from benzene to ethanol. Poly[1-phenyl-2-(4-vinylphenyl)-1,2-ethanedione-co-styrene] also designated as copolymer 4-vinyl benzil (VBZ) with styrene P (VBZ-co-S) containing on average 10 wt% (0.423 mol kg^{-1}) of VBZ with $M_w = 216$ kg mol^{-1} and $M_n = 113$ kg mol^{-1} was the same as in [16]. All solvents (analytical grade) were distilled prior to use.

*Characterisation of di(4-benzoylperoxide)ether (**BP-O-BP**) isolated from PS film after **BZ-O-BZ** photo-peroxidation.*

White crystals m.p. 136−139 °C;

Elemental analysis (C$_{28}$H$_{18}$O$_9$) calc. C 67.47; H 3.64; O 28.89; found C 67.50 H 3.60.

^{1}H NMR (CDCl$_3$): δ/ppm = 8.14, 8.12, 8.10, 8.08(2×d, 8 H), 7.69, 7.67, 7.66 (t, 2 H), 7.54, 7.53, 7.51 (t, 4 H), 7.17, 7.16 (d, 4 H).

^{13}C NMR (CDCl$_3$): δ/ppm = 163.1, 162.3 and 160.9 (2×C = O and C (ipso)-O), 134.3 (C para), 132.3, 129.8 and 128.9 (C arom.), 125.6 and 121.2 (2×Cipso), 119.3 (CH ortho to –O-).

FTIR (ATR): $\tilde{\nu}$/cm^{-1} = 3072, 2972, 2853, 1782 (C=O, peroxide), 1763 (C=O, peroxide), 1594 (C–H arom.), 1502, 1451, 1423, 1262, 1225, 1168, 991, 8468, 750, 699.

2.2. Instrumentation

FTIR spectra were recorded on a Nicolet Impact 400 spectrophotometer (Thermo Scientific, USA). NMR was measured using Varian 600 MHz NMR. Molar masses were determined by gel permeation chromatography (GPC) using THF as a mobile phase and consisting of Shimadzu HPLC pump LC-20, three PSS SDV 5 µm columns ($d = 8$ mm; $l = 300$ mm; 100 Å + 500 Å + 10^5 Å) and a refractive index detector (Shimadzu, Japan). Polystyrene standards (Polymer Standards Service) were used for calibration.

2.3. Polymer film preparation, irradiation, thermal treatment and swelling

Polymer films with thickness ~2 µm and ~6 µm consisting of
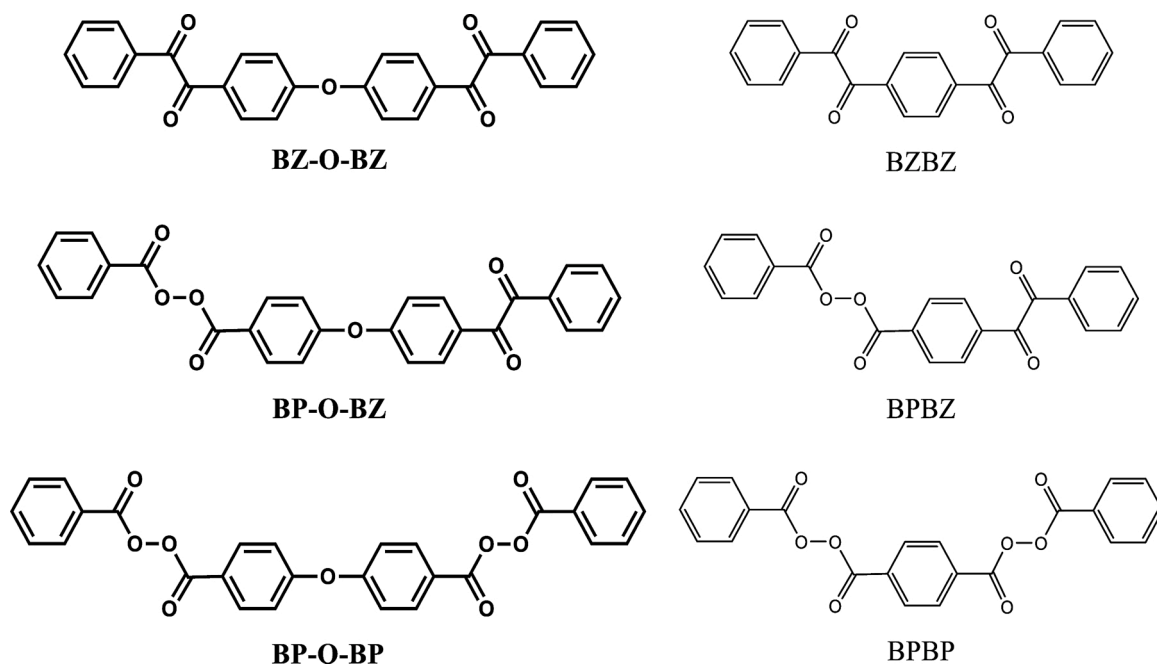
Scheme 1. Structures and abbreviations of starting 4,4′-oxydibenzil (**BZ-O-BZ**), assumed intermediate and final photo-peroxidation products studied in this work (left) compared with known 1,4-bisbenzil (BZBZ) (right).

~20 mg or ~60 mg, respectively, of **PS$_V$**, **PS$_N$** or **PS$_H$** and doped with BZ, BZBZ or **BZ-O-BZ** with good optical quality were prepared by casting from 1 ml (20 mg of PS) or 1.5 ml (60 mg of PS) of chloroform solutions onto a glass plate (10 cm^2 area). The plate was covered with a Petri dish to reduce the speed of the solvent evaporation. **PS$_H$** /**BZ-O-BZ** or **PS$_H$/ BP-O-BP** films with a precise concentration of the dopant (not thickness) were prepared by weighing the **PS$_H$** in the vials to which an appropriate volume of **BZ-O-BZ** or **BP-O-BP** in a chloroform solution was added to give the required concentration and adjusted to an equal volume (1 ml or 1.5 mL). After 24 h of careful PS dissolution, the solution was cast onto a glass plate. The self-supporting polymer films were separated from the glass plate by immersing in distilled water. The films were allowed to dry freely to a constant mass at ambient temperature for 24 h and subsequently under vacuum for 6 h. The films were then irradiated simultaneously at ambient temperature in a home-made carousel apparatus. The light source consisting of a 125 W medium-pressure mercury arc was placed into a tube with circulating water jacket which was surrounded by a 1 cm thick layer of a liquid filter (600 g NaBr and 12 g Pb(NO$_3$)$_2$ per 1000 ml of aqueous solution transmitting at λ > 340 nm). The distance of each sample (placed in rotating octahedron holders) from the arc was about 8 cm. A plastic filter foil (Solarzone film transmitting at λ > 400 nm, Hanita Coatings, Israel) was immersed in front of the sample. The film was exposed to radiation of an intensity of 8 mW cm^{-2}. Alternatively, in a later stage of this investigation, in all subsequent crosslinking experiments, the films were irradiated in a folded plastic filter foil (transmitting λ > 400 nm). Behind the irradiated films in a folded foil of a plastic filter, an aluminium foil was placed which reflected the unabsorbed light. Such a sandwich arrangement was attached on the most intensively irradiated area around the light-source tube. This simplified arrangement affords good results in a shorter time.

To extract a low-molecular weight photo-product from the PS matrix, the irradiated films were dissolved in chloroform and precipitated in methanol. The precipitation procedure was repeated 3 times. The precipitated polymers in the form of a film were characterized by FTIR. Methanol fractions resulting from the first precipitation were concentrated under reduced pressure and a crude product of about 20 % yield was obtained. The pure **BP-O-BP** was obtained following a chromatographic treatment on silica using toluene as an eluent and recrystallisation from a 1:1 chloroform: methanol mixture.

Thermal decomposition of both the peroxides (synthesised and added, and formed *in situ*) in PS films was conducted under normal air conditions and, in some cases, under vacuum, in sealed tubes at a constant temperature in the oven of a Shimadzu gas chromatograph. The films in the sealed tubes were separated with heat-resistant paper sheets to prevent the films sticking at elevated temperatures.

The insoluble fraction was determined by extraction with toluene at an ambient temperature. Since the gels used for the photo-peroxidation of **BZ-O-BZ** and subsequent peroxides decomposition, especially for **PS$_N$** and **PS$_V$** of a lower molecular mass, were voluminous, the films were soaked in toluene (15 ml per a sample) in closed bags made of a woven glass-fibre fabric. Similar results of gel content after 24 h and 194 h of extraction (Fig. SI-1 in Supporting Information) proved 194 h of extraction at ambient temperature to be sufficient. The bags with the residue of the film were removed from the toluene, and allowed to dry to a constant mass.

For the crosslinked **PS$_H$/BZ-O-BZ** polymer, the compact dry gels, after removal of the soluble part, were separated from the bags, immersed in toluene for 24 h to allow to swell, transferred to an aluminium foil and weighed once the solvent was removed from their surface. After drying to a constant mass, the dry gel mass was determined. Alternatively, the crosslinked gels after the decomposition of **BP-O-BP** in a swollen state (treated for one week in 15 ml of toluene) were transferred directly on to an aluminium foil and evaluated equally. Equilibrium degree of swelling DS_E was calculated by the equation:

$$DS_E = \frac{V_\infty}{V_0} = 1 + \frac{\rho_P}{\rho_S}\left(\frac{M_\infty}{M_0} - 1\right) \qquad (1)$$

where M_∞ is the mass of the swollen gel; M_0 is the mass of the dried gel; ρ_p is the density of the polymer (polystyrene $=1.05$ g mL^{-1}) and ρ_s is the density of the solvent (toluene $=0.865$ g mol^{-1}).

3. Results and discussion

3.1. Photo-peroxidation of BZ-O-BZ in PS film

In the preliminary experiments, the photochemical products of **BZ-O-BZ** in PS matrix were compared with the BZ and BZBZ structures which had undergone simultaneous irradiation under normal air conditions in a carousel apparatus at λ > 400 nm. The chemical changes were monitored by FTIR spectroscopy. As predicted, the changes in the FTIR spectra of **BZ-O-BZ** over the time showed a consumption of 1,2-diketones (1650−1700 cm^{-1}) accompanied by the formation of peroxides (1750−1800 cm^{-1}) (Fig. 1), as was the case for BZ and BZBZ. The rate of consumption of 1,2-diketo structures, estimated as described in work [31], was almost the same for all the compounds studied, reflecting similar reactivity of the 1,2-dicarbonyl groups in the photo-peroxidation reaction of the compounds in PS films. While BZ was transformed exclusively to BP [19] in the case of **BZ-O-BZ** a pronounced absorption near 1736 cm^{-1} and 1693 cm^{-1} became obvious after diketone consumption, suggesting the formation of ester and acid photo-products.

Both esters and acids bands were also observed in the BZBZ investigated previously [29], but the intensity of these bands in comparison with the peroxide bands for **BZ-O-BZ** was lower than for BZBZ. These two bands were attributed to benzoic acids and their esters structures formed from benzoyloxy radicals or their 4-substituted derivatives (Scheme 2). These radicals may be formed by decomposition of the BP structures intramolecularly sensitised by the BZ structures in the photo-peroxidation **BP-O-BZ** intermediate. While, in the case of BPBZ system formed from BZBZ, the energy transfer is quantitative, the decomposition of the previously-formed BP structure is also presumed to be quantitative [29]. The BZ-sensitised decomposition of the BP structures in the conjugated BPBZ and the oxygen-linked **BP-O-BZ** chromophores in the PS matrix appears to be similar to the benzophenone-sensitised decomposition of the BP structures in the condensed and the isolated chromophores in solution [32,33].
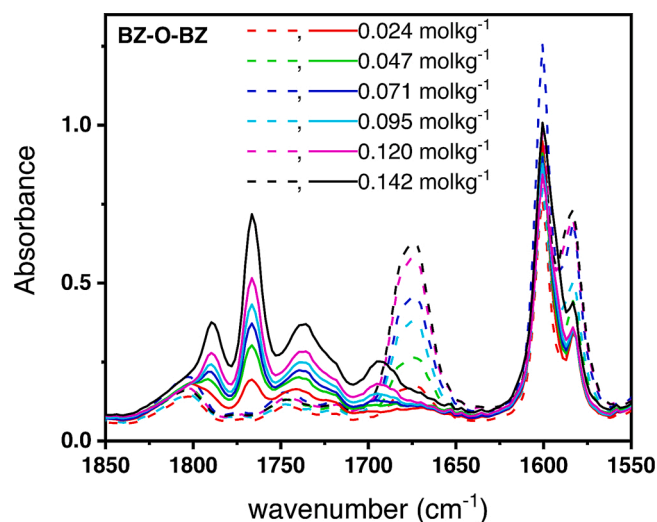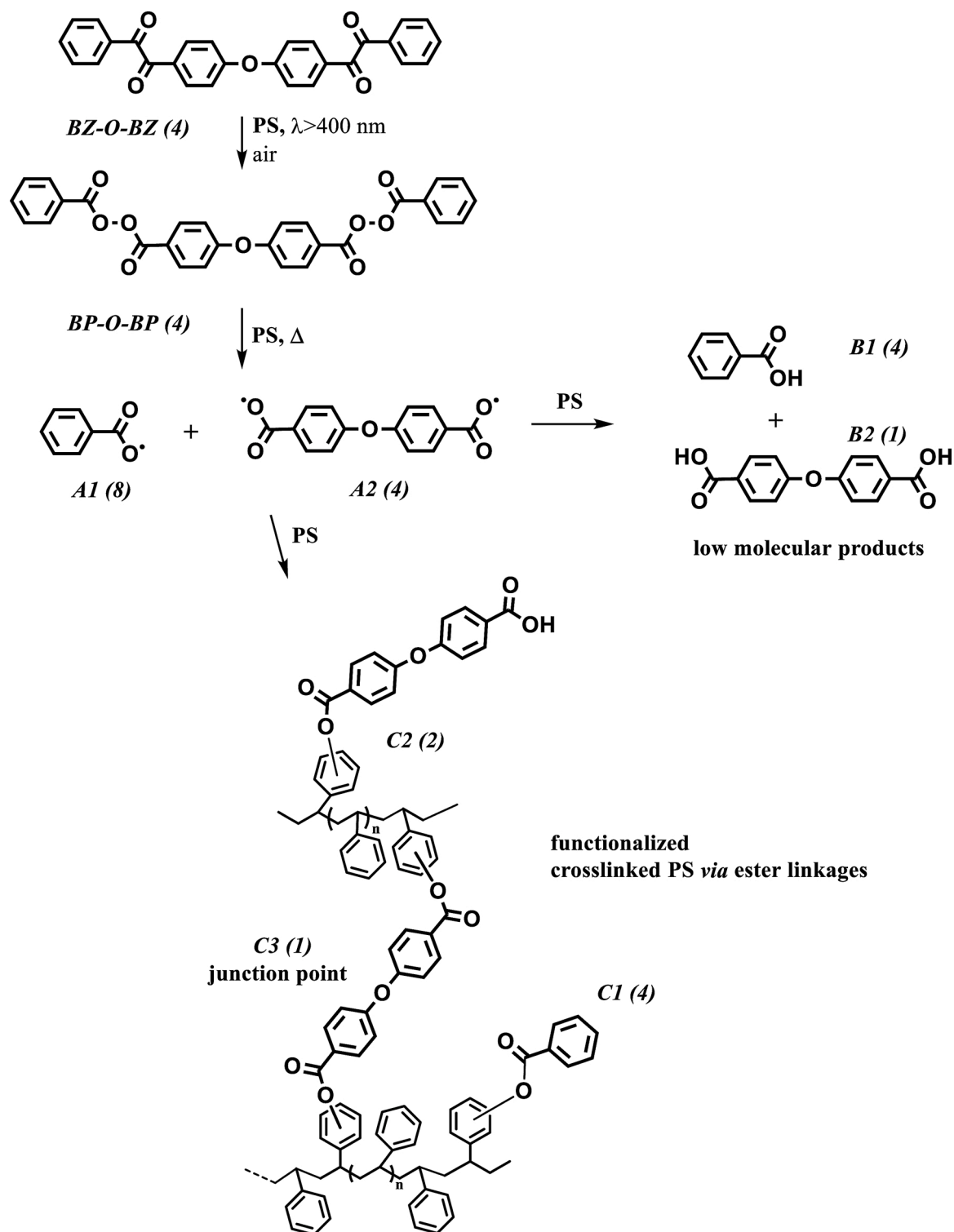

Fig. 1. FTIR spectra of different concentrations of BZ-O-BZ (0.024-0.142 mol kg^{-1}) in PS$_V$ films (~6 μm thick) not irradiated (dashed line) and irradiated (solid line) (48 h, λ > 400 nm, air).

Scheme 2. Simplified mechanism of PS crosslinking with freely added BP-O-BP or photochemically generated from BZ-O-BZ. The values in parentheses represent probabilities of emerging products and PS functionalities. The value (4) for BZ-O-BZ represents a theoretical value only.

Further information about photo-peroxidation was obtained after separation of the low-molecular compounds from the irradiated films. For this purpose, 0.375 mol kg^{-1} of **BZ-O-BZ** in the irradiated film was used. After the almost complete consumption of **BZ-O-BZ,** the irradiated films were dissolved in chloroform and precipitated in methanol. In Fig. 2 the FTIR spectra of the original film containing **BZ-O-BZ** are compared with the same film irradiated and films prepared from the precipitated irradiated polymer. The isolation of the presumed **BP-O-BP**

and its purification are difficult because of its low yield (25–30 %) and further crystallisation after its chromatographic separation. Despite all our efforts, only a small amount of **BP-O-BP** was isolated.

From the irradiated films, acids were removed completely, peroxides almost completely and esters in the prevailing quantity. On the other hand, the polymeric (insoluble) part contained only a small amount of peroxides and the remaining proportion of non-converted diketones both bound on PS chains probably *via* ester linkage. If the sensitised
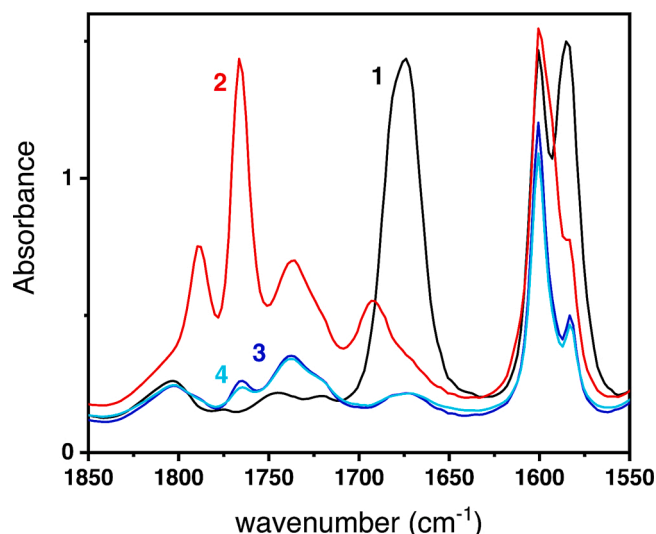
Fig. 2. FTIR spectra of BZ-O-BZ (0.375 mol kg^{-1}) in PS$_V$ film not irradiated (1) and irradiated to full conversion ($\lambda > 400$ nm, air) in a carousel (2) compared with 2 (3) and 3 times precipitated PS film (4).

decomposition of **BP-O-BZ** were efficient in the crosslinking, the portion of the peroxide bound to the PS capable of contributing to crosslinking in the subsequent thermal step would be higher. This is in conflict with the thermal [34] or also with the direct photochemical [35] decomposition of BP in PS. The efficient bonding of the benzoyloxy structures to PS in the thermal BP decomposition resulting in the formation of PS-benzoate has been known since the 1960s. The addition reaction is accompanied with the formation of benzoic acid. Hence, most probably either the esters and acids functionalities were formed as side-products during the peroxide formation, or the benzoyloxy radicals formed in the sensitised decomposition of BP structures in **BP-O-BZ** were unable to react with PS and were decomposed. This can be supported with the quenching of the triplet state of benzophenone by BP which affords nearly 80 % deactivation without cleavage of peroxide [36]. The lower absorption peak near 1740 cm^{-1} of the irradiated polymer film after precipitation, in comparison with that prior to precipitation, shows that a large portion of a low-molecular ester-like functionality was removed. A low-molecular ester-like functionality can be formed either from the side-products of the BZ structure photo-peroxidation or after decomposition of the BP structures and acyloxy radicals. Such deactivation of a bifunctional low-molecular dopant decreases the crosslinking yield. In the region around 1740 cm^{-1} the PS photo-oxidation products can also absorb [37, 38]. However, during the photo-peroxidation of BZ alone in PS, no absorption in the given region could be observed. Hence, the oxidation of PS photosensitised with the BZ structures can be excluded.

The photo-peroxidation in **BZ-O-BZ**/PS films led to small changes in the molecular characteristics of the polymer matrix as observed in the GPC traces (Fig. SI-2 in Supporting Information). Both chain scission and crosslinking are responsible for the dispersity broadening. These changes were visible mainly in the **PS$_N$** matrix with lower dispersity, where an increase in Đ from 1.35 to 1.56 was observed after 67 h of irradiation. While the average number molar mass M_n is decreasing by approx. 5 kg mol^{-1} representing degradation, the average weight molar mass M_w is increasing by approx. 10 kg mol^{-1} with the time of irradiation representing a macroradical recombination.

3.2. Thermal decomposition of in situ-formed BP-O-BP and doped PS films with synthesized BP-O-BP

The **BP-O-BP** structures, formed by prolonged photo-peroxidation in order to complete the consumption of **BZ-O-BZ** which was observed in FTIR spectra (Fig. 1), were thermally decomposed at 100 °C. The

complete decomposition of **BP-O-BP** was achieved after approx. 8 h. The FTIR spectra of the thermal decomposition products of the peroxides prepared photo-chemically under vacuum are shown in Fig. 3 left. In the FTIR spectra, the spectra of the irradiated films are partially overlapped by the spectra of the thermal products. Thus, in the thermally treated films, the initial spectra of the irradiated films are not included.

For comparison, the PS films which were doped with various concentrations of synthetically prepared **BP-O-BP** were also decomposed thermally under vacuum (Fig. 3 right).

The spectra of both **BP-O-BPs**, formed *in situ* by irradiation of **BZ-O-BZ** in PS films and the **BP-O-BP** synthetically prepared and added to PS films (Fig. 3), were similar after the thermal treatment. The only difference is the less pronounced shoulder near 1720 cm^{-1} related to aliphatic benzoates (denoted by line in Fig. 3). From the study of the side-products of the **BZ-O-BZ** irradiation (Fig. 2) and the efficient crosslinking with **BP-O-BP** (see below), the photochemically formed **BP-O-BP**, at a concentration lower than expected, provided lower concentrations of benzoyloxy radicals capable of reacting not only with the phenyl rings (Scheme 2), but also, to a lesser extent, with the aliphatic chain of PS resulting in the formation of aliphatic benzoates [34] which absorb in the 1720 cm^{-1} region. This reaction is probably responsible for the main chain scissions (Fig. 6).

The addition reaction of benzoyloxy radicals with the aromatic rings is rapid and reversible [39]. The small difference in the absorption co-efficients of phenyl benzoate and benzoic acids and the almost equal intensities of esters and acids bands after decomposition of the peroxide group in bis-peroxides suggests that the esters to acids molar ratio is also eq the esters to acids molar ratio is also equal. Hence, the counterpart, second acyloxy radical, was presumably acting as a scavenger of the aromatic hydrogen liberated from the phenyl ring during the substitution reaction of the benzoyloxy radical with the phenyl ring of PS [29]. This is supported by observation of the decomposition of BP in PS [34, 35] and with the 30–50 % addition reaction yield of 4-chlorobenzoyloxy radicals resulting from the decomposition of 4-chlorobenzoyl peroxide to PS [40]. The same decomposition is observed for phthaloyl peroxide in aromatic solvents [41].

On the basis of the present discussion, the simplified mechanism of the PS crosslinking with **BP-O-BP** or its precursor **BZ-O-BZ** was suggested (Scheme 2). The calculated probabilities of emerging products in Scheme 2 is based on presumed equal reactivity of two different acyloxy radicals formed quantitatively as well as from their equal ability to accept hydrogen or to joint to phenyl ring of PS. No reaction between molecules of additive was considered due to its low concentration in PS matrix. After decomposition of the BP moieties in **BP-O-BP**, two kinds of acyloxy radicals are progressively formed (products A1 and A2). Each acyloxy radical can be linked to the phenyl ring of PS or can scavenge a liberated hydrogen atom. Scavenging of the hydrogen atom leads to the formation of low-molecular benzoic acid (low-molecular products B1) and benzoic acid ether (low-molecular products B2). Binding to the phenyl ring yields polystyrene benzoate (functionalised PS C1) and polystyrene benzoate bearing the benzoic acid moiety (functionalised PS C2). Only the polystyrene benzoate bearing the BP moiety intermediate can cause the crosslinking in the next step. After decomposition of the linked BP moiety, the acyloxy radical counterpart reacts as in the previous case. It can be added to the aromatic ring or to scavenge a hydrogen atom. Only the addition of polymeric acyloxy radicals to the PS aromatic ring results in the crosslinking (junction point C3 in Scheme 2). This means that, theoretically, only half the number of polymeric acyloxy radicals may participate in the crosslinking. While two **BP-O-BP** are statistically required for the formation of one polymeric BP group, four **BP-O-BP** are theoretically required for one crosslink (junction point) in PS.

3.3. Influence of BZ-O-BZ concentration and PS type on gel content

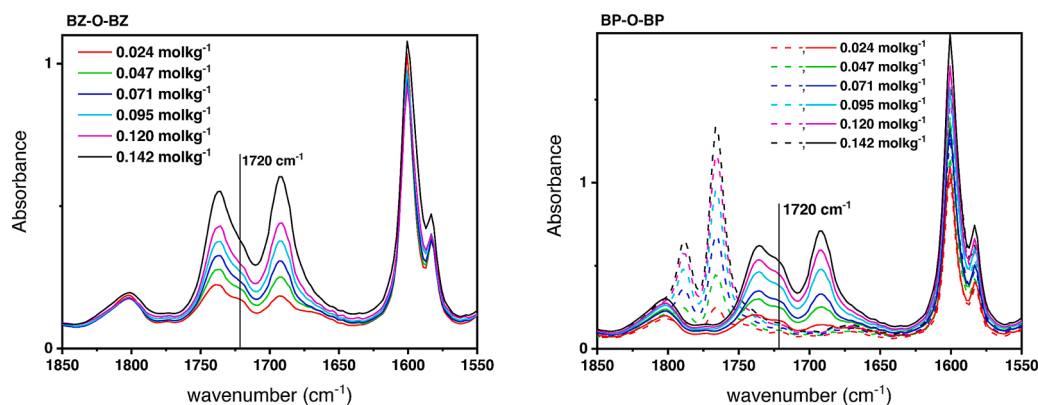A series of PS films containing different concentrations of **BZ-O-BZ**

Fig. 3. FTIR spectra of doped PS_V films (~6 μm thick): a) doped with different concentrations of **BZ-O-BZ** (0.024–0.142 mol kg^{-1}) irradiated (48 h, λ > 400 nm) under air and subsequently treated at 100 °C during 8 h in vacuum; b) doped with different concentrations of **BP-O-BP** (0.021–0.124 mol kg^{-1}) prior (dashed) and after (solid lines) treatment at 100 °C during 8 h in vacuum.

were irradiated by λ > 400 nm in air until the 1,2-dicarbonyl structures were fully consumed. The peroxides which were subsequently formed were fully decomposed thermally at 100 °C. The gel content was estimated as a fraction insoluble in toluene. With concentration of the **BZ-O-BZ** dopant up to 0.15 mol kg^{-1}, the gel content in PS_V attained approx. 70–80 %. The same experiments in PS_N led to a lower gel content and a low reproducibility of results. A gel content of almost 90 % was obtained with PS_H (Fig. 4). The gel content was calculated from the total weight of the film including the additive in order not to exceed the gel content value of 100 %. On the other hand, the presence of soluble low-molecular decomposition products from additives and a low-molecular fraction of PS contributed to a lower value of gel content. Since the highest concentration of **BZ-O-BZ** in Fig. 4 represents 10 wt% of PS_H and its conversion to **BP-O-BP** is only partial (see below), the decrease in gel content at a higher **BZ-O-BZ** concentration range can also be attributed to side-products of the **BZ-O-BZ** photo-peroxidation.

3.4. Evaluation of crosslinking and chain-scission yields

By the end of the photo-peroxidation of **BZ-O-BZ,** only small changes in the PS molar mass and their distribution were observed, as previously discussed. This may be due to hydrogen abstraction from the PS backbone by the excited BZ structures, or by the benzoyloxy radicals formed upon the decomposition of the BP structures formed in the **BP-O-BZ**

Fig. 4. Gel content after toluene extraction (194 h, 25 °C) of PS_H, PS_V and PS_N films (~ 6 μm thick) containing different concentrations of **BZ-O-BZ** irradiated for 48 h and subsequently heated at 100 °C for 8 h.

intermediate or in **BP-O-BP**. During the subsequent thermal decomposition of **BP-O-BP** in the PS matrix, extensive changes were observed, the most evident of which is the formation of an insoluble crosslinked polymer. In previous studies on BP-monoperoxide [34] and 4-chlorobenzoylperoxide BP derivative [40], only PS degradation accompanied by the benzoyloxy fragment binding to PS was reported. However, in the present study, the GPC traces of PS_N after BP thermal decomposition showed extensive degradation as well as some broadening towards higher-molar masses, suggesting some macroradicals combination (Fig. SI-3). To evaluate and compare the extent of degradation and crosslinking, a model thermal experiment was conducted deploying BP-monoperoxide in the PS_H matrix under conditions identical with those used for crosslinking.

As stated earlier, the crosslinking with **BP-O-BP** resulted primarily from the addition reaction of two bisacyloxy radicals, originated from one structure, to two phenyl rings of different PS chains. The simultaneous reaction of the acyloxy radical with the backbone produces radicals on the backbone and subsequent degradation of PS. Thus, the crosslinking competes with degradation of the PS matrix.

The ratio of the extent of the degradation processes to crosslinking is presumed to be constant and independent of the concentration of **BP-O-BP**. The ratio of the yields of scission and crosslinking (q_0/p_0) can be quantified from a Charlesby-Pinner plot (Eq. 2) [3,42,43] by determination of the intercept of linear fit on the y-axis. Eq. 2 applies to polymers with the "most probable" molar mass distribution ($Đ = 2$) and the equation is most frequently used for crosslinking by radiation.

$$s + s^{0.5} = \frac{p_0}{q_0} + \frac{1}{q_0 uD} \tag{2}$$

where s is the content of soluble fraction, p_0 is the average number of main chain scission per monomer unit and per unit dose, q_0 is the proportion of monomer unit crosslinked per unit dose, u is the initial number-average degree of polymerisation and D is the irradiation dose. In the case of chemical crosslinking, D is substituted with crosslinking agent concentration (Eq. 3). In the present case, the quantitative transformation of **BZ-O-BZ** to **BP-O-BP** is formally presumed.

$$s + s^{0.5} = \frac{p_0}{q_0} + \frac{1}{q_0 u[BP - O - BP]} \tag{3}$$

In Eq. 3, p_0 and q_0 are expressed per monomer unit and per concentration unit. In the present study, for simplicity, this equation was applied only to PS_H with the molar mass distribution $Đ = 1.96$ which is within the range of experimental error equal to the "most probable". The plot of the experimental data from the decomposition of **BP-O-BP** formed *in situ* from **BZ-O-BZ** in PS_H is shown in Fig. 5. A good linear fit ($R^2 = 0.992$) was obtained with an intercept for infinite concentration
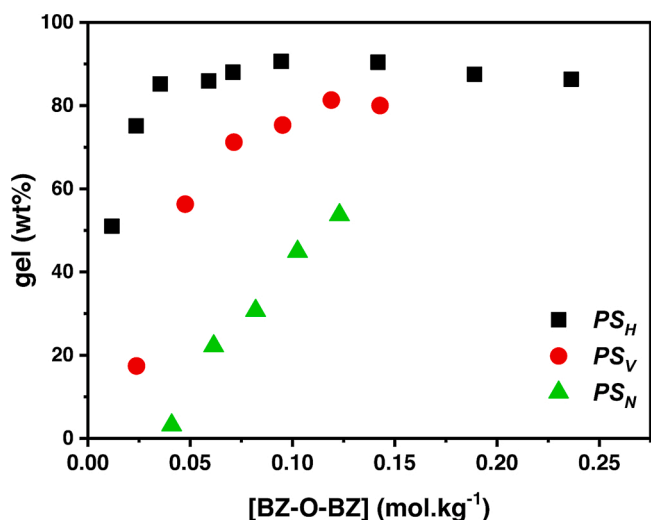
on the y-axis at 0.302 ± 0.027 and slope 0.0104 ± 0.0007 mol^{-1}kg. It is interesting to note that in this study the estimated $p_0/q_0 = 0.302 \pm 0.027$ is close to the value estimated for the crosslinking of PS by γ-radiation (0.35) [3]. The concentration of crosslinks $q_0 = 0.0222$ mol kg^{-1} monomer unit^{-1} was calculated from the slope corresponding to the quantitative transformation of **BZ-O-BZ** to **BP-O-BP**. Then the concentration of the average number of main chain scissions $p_0 = 0.00670$ mol kg^{-1} monomer unit^{-1} was obtained from the intercept. After multiplying the last value with *u,* the value 29.0 kg mol^{-1} of the main chain scissions of the average macromolecule per mole of **BZ-O-BZ** (**BP-O-BP**) was obtained. As the compound added contains two peroxide precursor structures, each peroxide structure is attributed a value of 14.5 kg mol^{-1}. With the BP (monoperoxide) and **PS$_H$** in the model experiment, the estimated value of the main chain scissions was 12.8 kg mol^{-1}. The agreement between the values is reasonable when assumptions and experimental errors are accounted for.

3.5. Crosslink density from swelling

The equilibrium degree of swelling DS_E was calculated based on the swelling in toluene (Eq. 1) for **PS$_H$** films treated identically as in the experiment summarised in Fig. 5. According to the Flory-Rehner Eq. 4, the real network molecular weight between crosslinks M_c can be calculated [44],

$$M_c = \left[\frac{2}{M_n} - \frac{1n(1 - DS_E^{-1}) + DS_E^{-1} + \chi DS_E^{-2}}{V_m \rho_p (DS_E^{-1/3} - \frac{DS_E^{-1}}{2})} \right]^{-1} \quad (4)$$

where V_m is the molar volume of toluene (106.3 ml mol^{-1}) and χ is the polymer-solvent interaction parameter of PS/toluene calculated [45] (value 0.36 was used). Because the gels obtained from **PS$_V$** were not sufficiently compact, the gel content was estimated in a closed bag facilitating the penetration of a solution only. A similar treatment of **PS$_H$** and different concentrations of **BZ-O-BZ** produced compact gels. Dry compact gels with good mechanical properties were removed from the bags (in some cases quantitatively) and allowed to swell in toluene. The calculated real network molar mass between crosslinks M_c and the crosslink density (concentration of crosslinks, concentration of junction points) $\nu_c = \rho_p/2M_c$ (where ρ_p is the density of PS equal to 1050 g dm^{-3}) is shown in Table SI-1. Assuming the formation of one crosslink from 4 molecules of an additive, the theoretical crosslink density was calculated. The estimated crosslink densities are compared with the theoretical values in Fig. 6. Theoretical crosslink densities with simultaneous
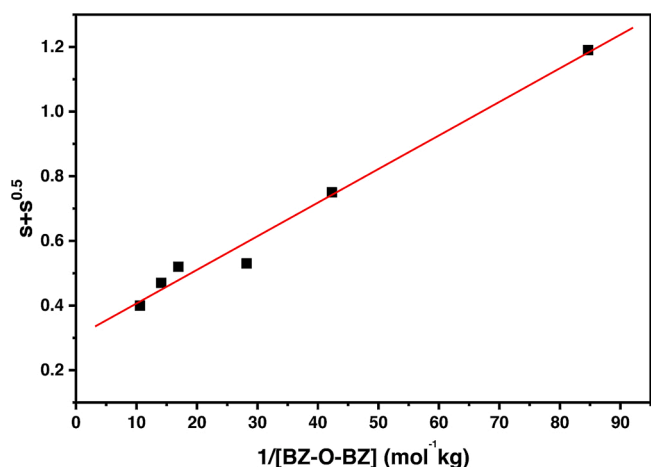
splitting (main chain scission of PS) were obtained by multiplying the concentration of theoretical crosslinks without scissions with the fraction of crosslinks. The fraction of crosslinks (0.768) was calculated from the concentrations resulting from the simultaneously proceeding main chain scissions ($p_0 = 0.00670$ mol kg^{-1} monomer unit^{-1}) and crosslinking ($q_0 = 0.0222$ mol kg^{-1} monomer unit^{-1}) obtained from the Charlesby-Pinner plot (Fig. 5).

The crosslink densities, within the range of experimental error, were independent of the variations in the experimental conditions, such as thickness of film (2 μm or 6 μm), temperature (100 °C or 120 °C) and the ambient atmosphere (air or vacuum) (Supporting Information Fig. SI-4).

The estimated crosslink densities represent approx. 25 % of the theoretical values which consider the degradation over the whole **BZ-O-BZ** concentration range. There are more possible explanations of the difference between experimental and theoretical values: i) the addition reaction of the benzoyloxy radical with PS may be less efficient than assumed; ii) the first acyloxy radical may be added more easily than the second, already bound to the polymer; iii) the side-products in non-selective transition of 1,2-dicarbonyl groups to peroxides are inactive in the crosslinking. In the latter case, the intermediate for the formation of side-products is not peroxide, or the benzoyloxy radical, its sensitized decomposition product, is less active in the substitution reaction with the PS phenyl ring at lower temperature.

To explain the discrepancy, the **PS$_H$** films with **BP-O-BP** synthesized were heated equally as **BP-O-BP** formed from **BZ-O-BZ** photochemically. The gel content and crosslinks densities were estimated for different concentrations of synthesized **BP-O-BP** (Fig. 7 and Table SI-2). The gel was formed quantitatively over the whole concentration range of **BP-O-BP** in the **PS$_H$**. matrix.

A quantitative acylation of benzoyloxy radicals formed from **BP-O-BP** on **PS$_H$** which participate in crosslinking under formation of equivalent of acid functions, for the first two to three values of the synthesized **BP-O-BP** concentration in Fig. 7 is in coincidence with the theoretical values. This justify the argument, that "four BP—O—BP are theoretically required for one crosslink (junction point) in PS" according to the mechanism suggested in Scheme 2. The only minor difference in the FTIR spectra of the crosslinked products formed from the synthesized **BP-O-BP** and **BP-O-BP** prepared *in situ* from **BZ-O-BZ** (Fig. 3) would also indicate the possibility of potentially equal crosslinking results in both situations. However, the comparison of experimental values in Fig. 6 and Fig. 7 shows that most probably only the **BP-O-BP** formed is active
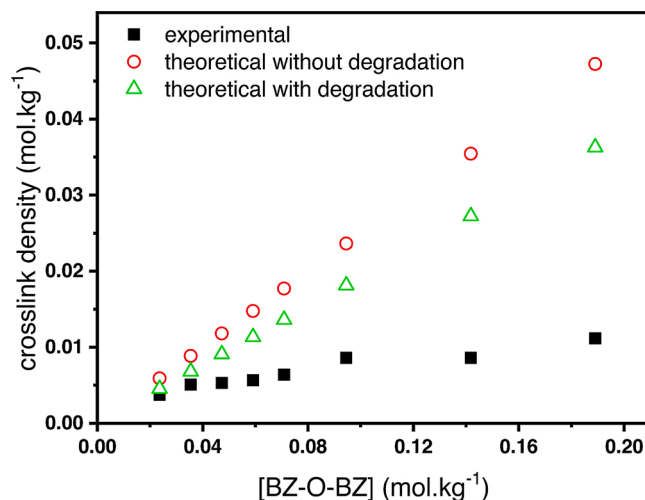
Fig. 5. Charlesby-Pinner plot for thermal decomposition (8 h,100 °C) of peroxides formed by irradiation (48 h, $\lambda > 400$ nm, air) of BZ-O-BZ in PS$_H$ film ($\sim$ 6 μm thick) extracted with toluene (194 h, 25 °C).

Fig. 6. Experimental and theoretical crosslink densities with and without considering main chain scissions in **PS$_H$** ($\sim$ 6 μm thick films) as a function of **BZ-O-BZ** concentration after irradiation (48 h, $\lambda > 400$ nm, air), thermal decomposition (8 h,100 °C) of peroxides and extraction with toluene (194 h, 25 °C). The last experimental point from Table SI-1 is omitted.
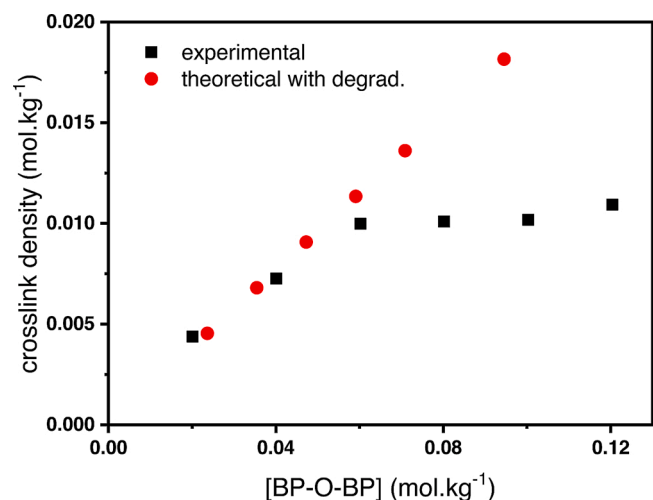
Fig. 7. Crosslink density of **PS_H** films (~2 μm thick) containing synthesized **BP-O-BP** obtained from the swelling experiment after thermal decomposition of peroxides (in air at 100 °C, 8 h) and extraction with toluene (194 h, 25 °C) compared with theoretical values.

in crosslinking, unlike the side-products in the non-selective photochemical transition of the 1,2-dicarbonyl group to peroxides that are less active or inactive in the crosslinking.

The crosslink densities are not increased with an increase in the **BP-O-BP** concentrations above 0.01 mol kg^{-1} (Fig. 7). This crosslink density corresponds to the M_c value of about 50.0 kg mol^{-1}. A similar effect was observed with crosslinking of the styrene copolymer *via* thermal azide-alkyne cycloaddition [13]. In this system, the cycloaddition-based cross-linking proceeded as a thermally-activated process to a critical reaction conversion (the concentration of the starting reactants remained unchanged), when the chain mobility became limited and

hindered the progress of the reaction. If this were to be the case in the crosslinking based on the decomposition of **BP-O-BP** in **PS_H** in the later stage, the network would prevent the accessibility of the acyloxy radical bound to the polymer and the PS phenyl ring. Any comparison of the PS crosslinking of **BP-O-BP** with the azide-alkyne cycloaddition entails a comparison of two different systems and does not satisfactorily explain the limit of crosslink densities of PS crosslinking with **BP-O-BP**.

In order to support the unambiguously suggested mechanism of PS crosslinking with peroxides and simultaneously to solve the problem of the preparation of hazardous peroxides, the thermal decomposition of the BP structures which were formed almost quantitatively (Supporting Information Fig. SI5) by photo-peroxidation of the BZ structures in copolymer, a 50 μm film of 4-vinyl benzil (VBZ) with styrene (P(VBZ-co-S)) was used. The only difference arising from using P(VBZ-co-S) rather than PS in crosslinking with **BP-O-BP** is the need to use half the concentration of reactant in the former case. The photochemistry and crosslinking of P(VBZ-co-S) was described previously [16], but the crosslink density is estimated only in the present study. Here, the crosslink density obtained experimentally from swelling after the generation and decomposition of peroxides (in P(VBZ-co-S) film irradiated with λ > 400 nm and thermally treated at 100 °C for 8 h) (Supporting Information Fig. SI5) was $\nu_c = 0.18$ mol kg^{-1} which corresponded to M_c = 3.0 kg mol^{-1}. According to the theory (Scheme 3), two VBZ structures are required for one junction point. Then, the theoretical crosslink density is half the concentration of VBZ in the copolymer which is equal to 0.21 mol kg^{-1} corresponding to the theoretical M_c = 2.48 kg mol^{-1}. Despite some possible degradation reaction, some BZ structures not converted to BP one and experimental error, the agreement between experimental (M_c = 3.0 kg mol^{-1}) and theoretical (M_c = 2.48 kg mol^{-1}) values is surprisingly good and also in agreement of the suggested mechanism (Scheme 3). The theoretical value M_c = 2.48 kg mol^{-1} correspond to the polymerization degree 23.8. For comparison for experimental M_c = 3.0 kg mol^{-1} the polymerization degree is 28.8.

While the crosslinking limit for P(VBZ-co-S) expressed by M_c = 3.0 kg
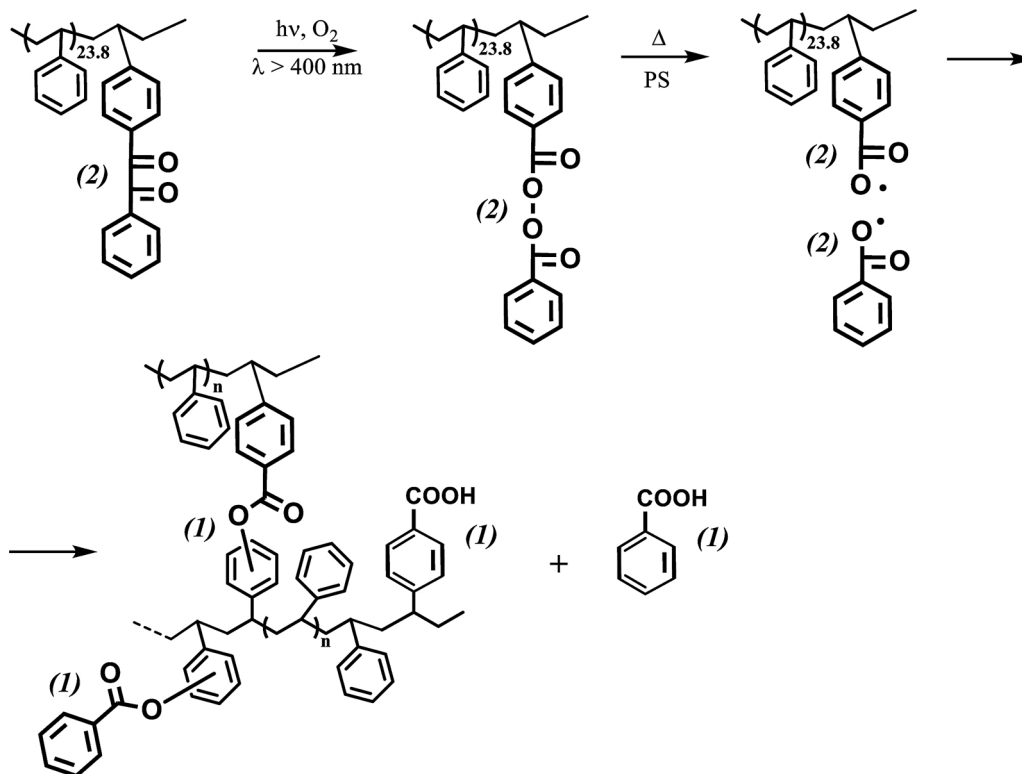
Scheme 3. Simplified mechanism of P(VBZ-co-S) copolymer photochemical generation of peroxides and crosslinking in film. The values in parentheses represent probabilities of emerging products.

mol^{-1} differs more than one order of magnitude as for PS with **BP-O-BP** ($M_c =50\,\text{kg mol}^{-1}$), the crosslink density cannot suppress crosslinking progress for high **BP-O-BP** concentrations. Hence, the crosslink density limit above 0.01 mol kg^{-1} in PS_H films observed as the departure from linearity in Fig. 7 at **BP-O-BP** concentrations of approximately 0.06 mol kg^{-1} is most probably due to the limited solubility of **BP-O-BP** in PS_H.

4. Conclusion

The thermal decomposition of 4,4′-oxybis(dibenzoyl peroxides) (**BP-O-BP**), synthetically prepared and added or formed photochemically *in situ* from 4,4′-oxydibenzil (**BZ-O-BZ**), yielded two benzoyloxy radicals in one structure responsible for the crosslinking of polystyrene (PS). During decomposition of the BP structure, the counterpart - the second acyloxy radical - acts as scavenger of an aromatic hydrogen atom released from the benzoyloxy-phenyl ring of the PS addition reaction intermediate. The binding of the benzoyloxy radicals to the PS phenyl ring by ester linkage resulted in the formation of equal amounts of an acid functionality. Hence, four structures of cross-linker are required for one junction point. Chain scission and crosslinking proceeded simultaneously. In accordance with the Charlesby-Pinner equation, the estimated ratio of the yield of the main chain scission to that of crosslinking was found to be approximately 0.3. For **BZ-O-BZ**, the estimated crosslink densities (after adjustment for degradation) corresponded to ~25 % of the theoretical concentrations of **BP-O-BP**. The crosslinking of PS with **BP-O-BP** synthetically prepared proceeded to a critical **BP-O-BP** concentration. A comparison of the PS crosslinking with **BP-O-BP** synthetically prepared with the decomposition of the BP structures formed photochemically quantitatively in the P(VBZ-co-S) led to the conclusion that it was the limited solubility of **BP-O-BP** in PS which was responsible for the crosslinking limit.

The lower crosslink efficiency of the **BP-O-BP** which results from photo-peroxidation of **BZ-O-BZ** in PS followed by thermal crosslinking in comparison with crosslink efficiency of the **BP-O-BP** synthesized and added to PS can be explained by the non-selective photochemical transformation of 1,2-dicarbonyl group in **BZ-O-BZ** to **BP-O-BP**. This produces side-products that are less active or inactive in the crosslinking. Although the crosslinking by the **BZ-O-BZ** photo-peroxidation products followed by their thermal treatment is less efficient than that achieved by the synthetically prepared BP—O—BP, it still results in the complete crosslinking of PS. In addition, the advantage of the system using the **BZ-O-BZ** is the high stability and easy handling when compared to **BP-O-BP**.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to legal or ethical reasons.

CRediT authorship contribution statement

Martin Danko: Conceptualization, Visualization, Writing - review & editing, Resources, Funding acquisition. **Jaroslav Mosnáček:** Conceptualization, Writing - review & editing, Resources. **Shiao-Wei Kuo:** Writing - review & editing, Resources. **Ivan Lukáč:** Conceptualization, Writing - original draft, Visualization, Investigation, Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jphotochem.2020.112849.

References

[1] D. López, G. Burillo, ACS Symposium Series 475 (1991) 262–270.
[2] W.W. Graessley, J. Phys. Chem. 68 (1964) 2258–2263.
[3] L.M. Alberino, W.W. Graessley, J. Phys. Chem. 72 (1968) 4229–4235.
[4] M. Yan, B. Harnish, Adv. Mater. 15 (2003) 244–248.
[5] M.P. Stevens, A.D. Jenkins, J. Polym. Sci.: Pol. Chem. 17 (1979) 3675–3685.
[6] T. Ueno, H. Shiraishi, S. Nonogaki, J. Appl. Polym. Sci. 29 (1984) 223–235.
[7] H.W. Gibson, F.C. Bailey, J.Y. Chu, J. Polym. Sci.: Pol. Chem. 17 (1979) 777–782.
[8] H. Morita, J. Photopolym, Sci. Technol. 4 (1991) 225–230.
[9] I. Gupta, S.N. Gupta, D.C. Neckers, J. Polym. Sci.: Pol. Chem. 20 (1982) 147–157.
[10] D.C. Neckers, J. Rad. Curing 10 (1983) 19.
[11] D.Y. Ryu, K. Shin, E. Drockenmuller, C.J. Hawker, T.P. Russell, Science 308 (2005) 236–239.
[12] R. Schinner, Ber. Bunsen. Phys. Chem. 102 (1998) 1710–1714.
[13] J.M. Spruell, M. Wolffs, F.A. Leibfarth, B.C. Stahl, J. Heo, L.A. Connal, J. Hu, C.J. Hawker, J. Am. Chem. Soc. 133 (2011) 16698–16706.
[14] C. Kósa, I. Lukáč, R.G. Weiss, Macromolecules 33 (2000) 4015–4022.
[15] J. Mosnáček, R.G. Weiss, I. Lukáč, Macromolecules 35 (2002) 3870–3875.
[16] J. Mosnáček, R.G. Weiss, I. Lukáč, Macromolecules 37 (2004) 1304–1311.
[17] B. Husár, I. Lukáč, J. Photochem, Photobiol. A: Chem. 195 (2008) 191–197.
[18] B. Husár, S. Commereuc, Š. Chmela, V. Verney, Polym. Int. 59 (2010) 1563–1570.
[19] J. Mosnáček, I. Lukáč, Š. Chromik, I. Kostič, P. Hrdlovič, J. Polym. Sci., Part A: Polym. Chem. 42 (2004) 765–771.
[20] I. Lukáč, C. Kósa, Macromol. Rapid Commun. 15 (1994) 929–934.
[21] C. Kósa, I. Lukáč, R.G. Weiss, Macromol. Chem. Phys. 200 (1999) 1080–1085.
[22] J. Mosnáček, K. Borská, M. Danko, I. Janigová, Mater. Chem. Phys. 140 (2013) 191–199.
[23] H. Simbürger, W. Kern, K. Hummel, C. Hagg, Polymer 41 (2000) 7883–7897.
[24] K. Nagakubo, F. Akutsu, T. Uchiyama, S. Sato, M. Miura, Polymer 23 (1982) 342–344.
[25] J. Mosnáček, I. Lukáč, M. Bertoldo, F. Ciardelli, Chem. Pap. 67 (2013) 9–17.
[26] N. Grassie, J. Gilks, J. Polym. Sci.: Polym. Chem. Ed. 11 (1973) 1531–1552.
[27] S.X. Cai, J.C. Nabity, M.N. Wibourne, J.F.W. Keana, Chem. Mater. 2 (1990) 631–633.
[28] M. Yan, M.N. Wybourne, J.F.W. Keana, React. Funct. Polym. 43 (2000) 221–225.
[29] I. Lukáč, C. Kósa, B. Husár, Macromol. Chem. Phys. 215 (2014) 171–176.
[30] I. Lukáč, B. Husár, C. Kósa, J. Fáryová, International application PCT/SK (2014), 050008.
[31] I. Lukáč, C. Kósa, R.G. Weiss, Photochem. Photobiol. Sci. 8 (2009) 1389–1400.
[32] J.E. Leffler, An Introduction to Free Radicals, J. Wiley, New York, 1993, p. 133.
[33] J.E. Leffler, J.W. Miley, J. Am. Chem. Soc. 93 (1971) 7005–7012.
[34] H.C. Haas, J. Polym. Sci. 54 (1961) 287–299.
[35] V.P. Pustoshnyi, Yu.A. Mikheyev, D.Ya. Toptygin, Polymer science U.S.S.R. 1983, 25, 1504-1512, Vysokomol. Soed. A25 (1983) 1295–1301.
[36] K. Tokumaru, Res. Chem. Intermed. 22 (1996) 255–273.
[37] B. Mailhot, J.-L. Gardette, Macromolecules 25 (1992) 4119–4126.
[38] B. Mailhot, J.-L. Gardette, Macromolecules 25 (1992) 4127–4133.
[39] J. Saltiel, H.C. Curtis, J. Am. Chem. Soc. 93 (1971) 2056–2058.
[40] J.W. Breitenbach, H. Frittum, J. Polym. Sci. 29 (1958) 565–571.
[41] Ch. Yuan, Y. Liang, T. Hernandes, A. Berriochoa, K.N. Houk, D. Siegel, Nature 499 (2013) 192–196.
[42] A. Charlesby, S.H. Pinner, Proc. R. Soc. Lon. Ser.-A A249 (1959) 367.
[43] A. Shyichuk, G. Tokaryk, Polymery 50 (2005) 219–221.
[44] P.J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, 1953.
[45] J. Brandrup, E. H. Immergut, E. A. Grulke, Ed., Polymer Handbook, 4-th Ed. VII, p. 707.