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

B. Husár, I. Lukáč *

Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, Slovakia

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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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* Corresponding author. Tel.: +421 2 54777404; fax: +421 2 54775923.
E-mail address: ivan.lukac@savba.sk (I. Lukáč).

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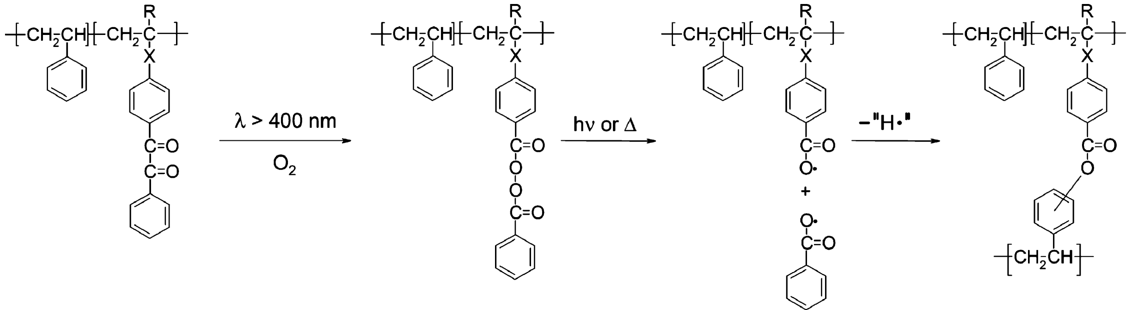
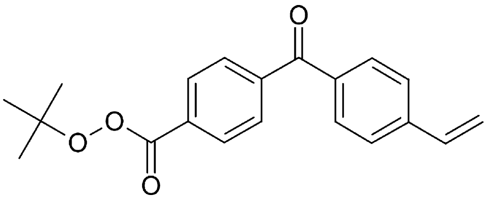


a) X = CO-O-CH_2-CH_2-O; R = CH_3 [12]
b) X = CO; R = H [13]
c) X = chemical bond; R = H [14]
d) X = 4-C_6H_4-CH_2-O-CH_2-CH_2-O; R = H (BzS/S - present work)

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). ^1H 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_4NBr (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