



Oxidative photopolymerization of thiol-terminated polysulfide resins. Application in antibacterial coatings



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ABSTRACT

A UV photoinduced cross-linking of non-modified commercial poly(disulfide) resins (Thioplast) is reported via the air oxidative photocoupling of terminal thiol functions. Catalyzed by a photogenerated guanidine base (TBD), this step-growth photopolymerization is useful to maximize disulfide functions content. The mechanism proceeds through thiol deprotonation into thiolate anions, further oxidized into thiyl radicals, eventually dimerizing into disulfide cross-links. Starting with a detailed structural characterization of the thiol-terminated resin, photooxidative kinetics are studied under exposure to a polychromatic medium-pressure Hg arc using Raman and infrared spectroscopy. The effects of irradiance, film thickness, photobase concentration, resin molar mass, and content of an additional polythiol monomer (reactive diluent) have been investigated. In an effort of upscaling, irradiation under a 365 nm LED panel has enabled the fast preparation of 1.5 μm thick cross-linked poly(disulfide) coatings in a matter of minutes. Capitalizing on the ability of residual thiol groups to react with silver cations, a post-functionalization has been successfully performed, leading to films exhibiting at their surface stable thiolate-silver bonds as proved by X-ray photoelectron spectroscopy. Despite the well-established biocide action of silver ions, no antibacterial action has been evidenced by confocal fluorescence microscopy because of insufficient release.

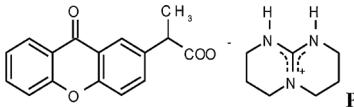
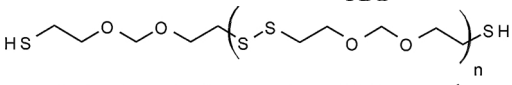
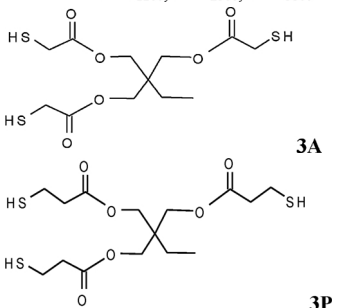
1. Introduction

Discovered as early as in the 1920s, poly(disulfide) (PdS) was the first synthetic rubber to be marketed in the United States [1,2]. After having initially drawn great attention as a substitute for natural rubber in tires production, this target application was gradually left in favor of more suitable polymers such as polybutadiene and its derivatives [3]. The main obstacles to a large scale utilization of PdS included processability issues, thermal instability and insufficient mechanical properties as regards to compression and abrasion. Nevertheless, PdS elastomer has flourished in niche markets including technical joints for aerospace, construction and double glazing [4]. Four distinctive properties make it particularly attractive for these specific applications: impermeability to water vapor, high resistance to solvents, durability, and low temperature flexibility. Commercial development has been driven by two major achievements: firstly, the development of a preparation method to low-molecular weight liquid PdS oligomers – often referred to as *polysulfide prepolymers* or *Thiokol*[®] – having internal

disulfide bonds, and containing at least two thiol functions: HS-(R-SS)_n-SH. The oxidation of SH groups into SS bonds remains today the major reaction pathway to induce cross-linking. Secondly, the development of PdS oligomers based on bis(ethyl)formal (R = CH₂CH₂OCH₂OCH₂CH₂) providing optimum properties to the final elastomer (see structure in Table 1) [5,6]. In most cases, the cross-linking requires 2-component formulation in order to separate the oxidizing agent and the prepolymer [7]. In addition, the base-catalyzed oxidation reaction is slow (on average, between 1 h–24 h), and requires a high concentration of oxidant (4–12 wt%) which may impact the final properties [8]. Finally, the applications are limited to structural materials such as seals, and the perspective of developing PdS coatings has been scarcely explored [9]. Yet, a high concentration of SS functions could confer to the final film specific characteristics [10] such as barrier properties, dynamic behavior, increased refractive index and broadened transparency in the infrared region. In addition, residual thiol groups might make feasible a surface post-functionalization through efficient reactions such as thiolene, thiol-Michael or thiol-electronically excited carbonyl compounds

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Table 1
Chemical structures of the compounds used in this study.

Type	Structure
Photobase generator	
PdS oligomer	
Polythiol monomer	

[11].

UV curing is currently one of the fastest growing technologies for the eco-efficient production of polymer coatings [12]. The process starts from a liquid film based on a one-component formulation including a photoinitiator as well as a mixture of multifunctional oligomers and monomers. Exposure to UV-vis radiation induces usually a chain-growth polymerization, yielding eventually a thermoset film [13]. The effectiveness of this method relies on a unique combination of features: absence of organic solvent, reaction at room temperature, short cycle times and small-scale production lines. The use of radiation as a stimulus to trigger the polymerization of PdS resin has been rarely reported in the literature [14–16]. In all cases, thiol terminal groups of PdS resins were subjected to chemical modification. In the 1990s, Morton Inter. Corp. (previously known as Thiokol Chemical Corporation) manufactured several acrylate-terminated polysulfide oligomers. However, the change from a step-growth mechanism to a chain-growth one led to a higher cross-linking density, that caused the properties of the material to deteriorate substantially [14]. In 2003, several photoactive carbonyl end-groups were introduced by Caddy et al. [15]. Mechanistically, ketone groups reacted from their first triplet state ($^3(n, \pi^*)$ -state) and abstracted hydrogen from additional thiol species (RSH) acting as reducing molecules (co-initiator). A cross-linked disulfide was assumed to form through recombination reactions involving the photogenerated thiyl radicals ($RS\cdot$). However, several dozens of hours of UV irradiation were necessary to obtain a solid film. Very recently, Brei et al. introduced terminal alkene groups onto polysulfide resins, thereby enabling them to be photocured via a more efficient radical thiol-ene reaction. Allyl and methallyl-terminated PdS oligomers were synthesized and reacted with polythiol monomers or thiol-terminated PdS oligomers. The resultant solid elastomeric films were tested as adhesives for a target use in aircraft [16]. Good adhesion properties were achieved on various metallic substrates, but only after the incorporation of an organosilane, 3-mercaptopropyl)trimethoxysilane, playing the role of adhesion promoter.

We report herein an alternative photoinduced cross-linking process using non-modified commercial thiol-terminated PdS resins (Table 1), and based on the oxidative photocoupling of SH functions into disulfide. In contrast to previous reports, keeping the step-growth polymerization mechanism should maximize the disulfide functions content and allow retention of the excellent properties of poly(disulfide)

materials. Radiation control of polymerization relies on the photo-generation of a superbase catalyst (1,5,7-triazabicyclo[4.4.0]dec-5-ene: TBD) through a photobase generator (xanthone propionic acid-protected TBD, PBG, see Table 1) [17]. Using this PBG, we have recently demonstrated the feasibility of multiple thiol air oxidation of polyfunctional thiol monomers to yield disulfide cross-linked films [18,19], but the photooxidative polymerization of PdS resin is unprecedented. In terms of mechanism, given that thiols are more acidic than alcohols by an average of about 5 pK_a units (pK_a = 5–11), TBD (pK_a ≈ 13.5) can readily react with a thiol to form a thiolate anions RS^- acting as a much better electron donor [20]. This shift enables oxidation reaction by atmospheric oxygen to form thiyl radicals. Subsequent dimerization of thiyl radicals to disulfide ($RS-SR$) results in cross-linking. Because oxidation is ensured by atmospheric oxygen, the issue of UV attenuation from conventional inorganic oxidizing agents dispersed as particles (MnO_2 , $NaBO_2 \cdot H_2O_2$, $Na_2Cr_2O_7$) is circumvented.

We start with a detailed structural characterization of the PdS resin (Table 1) using liquid ^{13}C and 1H NMR spectroscopy. The kinetics of photooxidative curing for a 1.5 μm -thick PdS-based sample were studied by Raman and infrared spectroscopy under different experimental conditions as regards to irradiance, film thickness, PBG concentration, molar mass of PdS resin, and the content of an additional polythiol monomer behaving as reactive diluent (see structure in Table 1). For these optimization experiments, a polychromatic medium-pressure Hg arc ($\lambda > 330$ nm) was employed whose focused radiation enabled only small samples' preparation. In an effort of upscaling, an LED array providing a monochromatic radiation at 365 nm made possible the rapid production (3 min) of solid cross-linked PdS coatings on large surfaces. The structure of the insoluble photopolymer was examined by ^{13}C solid-state NMR. Capitalizing on the ability of residual thiol groups to react with silver cations, a post-functionalization was performed to form films exhibiting at their surface stable thiolate-silver bonds as proved by X-ray photoelectron spectroscopy (XPS). Assuming the biocidal action of silver ions possibly released from the films, their anti-bacterial properties were assessed in presence of bacterium *Escherichia coli* through confocal fluorescence microscopy.

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