



Thiolactone-based polymers for formaldehyde scavenging coatings

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ABSTRACT

A novel, straightforward chemical platform to prepare polymers with covalently bound amine functional groups has been developed for applications as coatings that scavenge formaldehyde emissions. For the polymer preparation, an amine-thiol-ene conjugation process was used to combine N-(allyloxy)carbonyl homocysteine thiolactone monomer with different amines, which simultaneously released a thiol group for subsequent thiol-ene radical polymerization. Results of the European standard formaldehyde release test by the flask method indicated that the obtained polymers with higher amine loadings resulted in a greater reduction in formaldehyde concentration. Urea-formaldehyde adhesive was overcoated with scavenging polymers, which resulted in a significant reduction in formaldehyde emissions. The amine-functionalized polymers were characterized by NMR and DSC before and after exposure to formaldehyde. After exposure to formaldehyde, polymers exhibited additional proton peaks in the NMR spectra and their glass transition temperature increased, which implied that formaldehyde was bound to the polymers.

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1. Introduction

Smart coatings comprise a broad range of advanced coatings with multifunctional properties, such as self-healing, self-cleaning, superhydrophobic, stimuli-responsive, and antifouling [1]. Traditional protective coatings form a passive barrier that shields the substrate from environmental damage. In contrast, smart coatings typically contain active components in the polymer resin or additives that impart additional properties to coatings. The active components in coatings enable them to interact with environmental stimuli, such as pH, UV light, temperature, mechanical impact, or oxygen [2]. For example, smart barrier coatings in food packaging contain oxygen scavengers that actively trap oxygen, which prevents food spoilage and extends shelf-life [3]. Scavenging coatings are valuable in many applications for the reduction of undesired chemical species, such as volatile compounds [4], radicals [5], corrosive agents [6], and moisture [7]. For the development of advanced coatings, techniques for introducing different scavenging functionalities into polymers are necessary.

Formaldehyde is an indoor air pollutant that can cause respiratory irritation and cancer after long-term exposure [8]. The International Agency for Research on Cancer (IARC) classified formaldehyde as carcinogenic to humans [9], which led to stricter regulations on the emissions of formaldehyde. The recommended limit for formaldehyde in residential indoor air

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was established at 0.1 mg/m^3 or about 0.08 ppm by the World Health Organization (WHO) [10]. Many countries, such as Japan and the United Kingdom, have also adopted the 0.1 mg/m^3 limit [8]. Mass production of urea formaldehyde adhesives for medium density fiberboard, particleboard, and plywood resulted in a need for formaldehyde abatement.

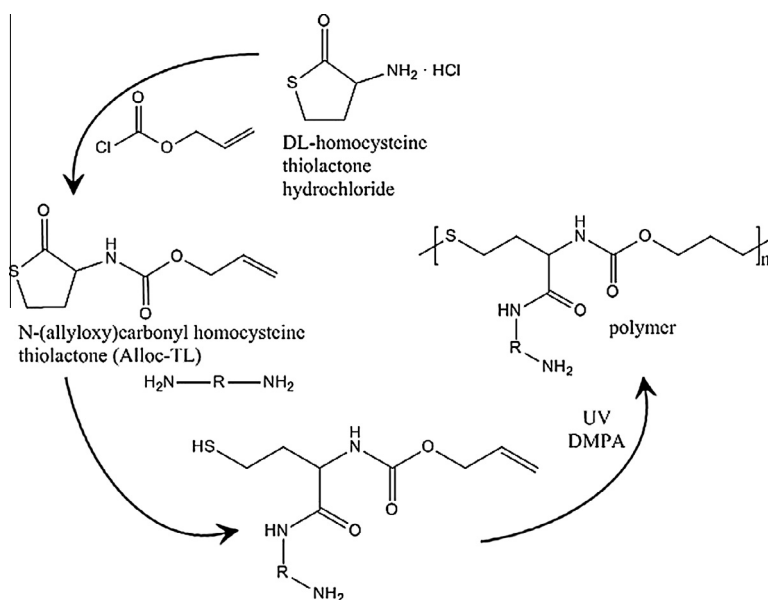
Research efforts have been directed towards reduction of formaldehyde by reformulation of resins and incorporation of formaldehyde scavengers. In this respect, different additives have been investigated for formaldehyde scavenging, including chemical agents (eg. sodium metabisulfite, ammonium bisulfite) [11] and natural components (eg. wheat flour, tannin, rice husk and charcoal) [12]. Compounds with amine groups can be effective in scavenging formaldehyde, since amines undergo an addition reaction with formaldehyde forming methylol groups, which can react further to form methylene bridges [13]. The effectiveness of amines in formaldehyde scavenging depends on several parameters, including the amount of amine groups in the matrix, the structure of the amine compound, and the morphology of the matrix.

Boran et al. determined that the emission of formaldehyde from medium density fiberboard panels, fabricated with urea formaldehyde resins, decreased with the addition of urea, propylamine, methylamine, ethylamine, or cyclopentylamine solution to the resin [14]. Addition of amine compounds led to an increase in water absorption and thickness swelling values of fiberboard. Medium density fiberboard panels with added amines exhibited higher internal bond strength, modulus of rupture, and modulus of elasticity. Therefore, scavenging additives can have an impact on the properties of the resin, which may be undesirable for certain applications. Nomura and Jones impregnated polymeric amines, such as branched poly(ethyleneimine), linear poly(ethyleneimine), and poly(allylamine) into mesoporous silica for the adsorption of airborne formaldehyde [15]. The formaldehyde adsorption capacity increased in proportion to the amount of amines, with maximum capacity corresponding to almost filled pores with slight residual porosity.

In contrast to the previous strategies of addition of formaldehyde scavengers to materials, our research aimed to use thiolactone chemistry for the covalent linkage of scavenging functional groups to a polymer backbone and the resulting polymer thin film. This strategy could be effective for formaldehyde abatement in a wide range of products and applications without the need to reformulate existing resins. In addition, incorporation of scavenging functionalities by covalent linking to the polymer backbone is expected to reduce undesired migration and loss of scavengers over long time periods.

Thiolactone chemistry has been established earlier as an effective method for one-pot multi-step synthesis of multifunctional polymers [16]. In previous research, thiolactone chemistry has been demonstrated as an effective strategy for the preparation of isocyanate-free polyurethanes [17], diversely substituted polyamides [18], hyperbranched polymers [19], functionalized cyclic polymers [20], glycopolymer nanoparticles [21], poly(thioetherurethane)s [22] and crosslinked chitosan polymers [23].

DL-homocysteine thiolactone hydrochloride is a renewable and commercially available heterocyclic thioester with a protected thiol group. An AB' monomer containing a double bond and a thiolactone unit has been synthesized by the addition of allyl chloroformate to DL-homocysteine thiolactone hydrochloride to form N-(allyloxy)carbonyl homocysteine thiolactone (Alloc-TL) (Scheme 1). Polymers with different functional groups have been prepared from the Alloc-TL monomer, following the earlier described amine-thiol-ene conjugation [16]. Addition of primary amine compounds to Alloc-TL results in thiolac-



Scheme 1. Reaction of DL-homocysteine thiolactone hydrochloride and allyl chloroformate to form N-(allyloxy)carbonyl homocysteine thiolactone (Alloc-TL) monomer, followed by aminolysis and thiol-ene reaction in the presence of 2,2-dimethoxy-2-phenyl acetophenone (DMPA) photoinitiator and UV light.

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