Reactive & Functional Polymers 71 (2011) 195–203

Contents lists available at ScienceDirect

Reactive & Functional Polymers

journal homepage: www.elsevier.com/locate/react

ROMP polymer-based antimicrobial films repeatedly chargeable with silver ions

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ARTICLE INFO

Article history:
Received 19 October 2010
Received in revised form 1 December 2010
Accepted 1 December 2010
Available online 5 December 2010

Keywords:
ROMP
Ag–polymer complex
Bactericidal film

ABSTRACT

Two norbornene derivatives bearing a pendant pyridyl group were prepared: the 3-(pyridin-2-yl)propyl ester of 5-norbornene-*endo*-2-carboxylic acid (**1**) and *N*-(pyridin-2-ylmethyl)-5-norbornene-*endo*-2,3-dicarboxyimide (**2**). Both of these compounds produced high yields of ROMP polymers, poly(**1**) and poly(**2**), with the 2nd generation Grubbs catalyst. When Ag^+ ions were added to these polymer solutions, the polymer–Ag^+ composites, poly(**1**-Ag) and poly(**2**-Ag), were formed quantitatively. Poly(**2**) and poly(**2**-Ag) produced films from their DMF solutions, and the latter film showed strong antimicrobial properties against Gram-positive *Bacillus subtilis* and Gram-negative *Escherichia coli*. Alternatively, when the film of poly(**2**) was immersed in a solution of Ag^+, it was able to trap the ion to give a surface-modified film [Ag/poly(**2**)]. The antimicrobial efficacy of [Ag/poly(**2**)] was the same as that of films made of poly(**2**-Ag), which indicated that the solid-state reaction of the film surfaces toward Ag^+ ions in solution was quantitative. When the [Ag/poly(**2**)] film lost its biocidal effect after repeated use, the Ag^+ ions could be reloaded by immersing the film in a silver ion solution, which fully restored original activity.

1. Introduction

The use of silver as an antimicrobial agent has been known for centuries, and silver still plays an important role in a variety of medical and health care systems [1,2]. As synthetic polymer materials, e.g., plastics and textiles, are becoming ubiquitous in our modern life, the protection of polymer surfaces from microbes (fungi, bacteria, and viruses), which not only cause staining and odors but also could mediate infection, has become an important issue. The need for biocidal additives to polymers has been predicted to continue to increase, driven primarily by consumer awareness regarding hygienic surfaces.

Most silver-containing antimicrobial polymer materials consist of dispersed nanoparticles of elemental silver. Typically, they are prepared by the *in situ* reduction of silver ions in a polymer solution and successive evaporation of the solvent to obtain a solid or film of the composite [3]. Sparingly soluble colloidal silver bromide/polymer composite has also been proposed to realize steady and improved bioactivity [4,5]. A problem with polymer–silver hybrid solids of this type is that only the particles exposed on the polymer–solid surfaces can be effective, while those within the solid bulk can have no effect unless the polymer matrix degrades. To localize silver nanoparticles only onto solid surfaces, their direct deposition on preformed polymer solids has been studied [6–8]. In some cases, porous polymer surfaces have been used to mechanically hold the silver particles [9–11]. The antimicrobial efficiency should depend on the size of the silver particle [3a,4], which is often not uniform and is governed by various factors, such as the reduction/aggregation rate of silver and the chemical nature of the polymer matrix.

Another, albeit less common, strategy is to release Ag^+ ions from polymer-bound complexes of otherwise very water-soluble silver ions. Examples of polymer side chains that can coordinate to Ag^+ ion include sulfides [12], triethylenetetramine [13], and sulfadiazines [14]. All polymer matrices in this category described so far are prepared from monomers that are polymerizable via radical initiators because those monomers with a pendant strongly coordinating Lewis base are generally difficult to polymerize by transition metal-catalyzed coordination polymerization. In general, the antibacterial efficiency of Ag^+ ion-containing polymers is lost more readily than that of polymers containing Ag metal nanoparticles due to the faster leaching out of Ag^+. It may be possible to overcome this drawback if the polymer solid can repeatedly reload Ag^+ ions.

Recently, transition metal-catalyzed ring-opening metathesis polymerization (ROMP) has emerged as a new type of industrially applicable process to produce materials for a variety of products such as bathroom fixtures, ballistic panels, and large equipment body parts [15]. Therefore, it is highly desirable to develop methodologies that would make it possible to fix silver on ROMP polymer matrices in a controllable manner. We report here that ROMP

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doi:10.1016/j.reactfunctpolym.2010.12.001

is possible for NB (NB = norbornene or bicyclo[2,2,1]hept-2-ene) monomers with pendant 2-pyridyl groups. A related ROMP polymer of a NB derivative functionalized with *N,N*-di-2-pyridylamide was prepared using Schrock's catalyst and the resulting polymer beads were used for the selective extraction of mercury and palladium ions [16]. The polymer with a 2-pyridyl group reported here could form a film, and its surface could fully trap Ag^+ when the film was fully immersed in a solution of silver ions. The extent of this trapping was confirmed chemically and assessed biologically on a molecular basis. The antimicrobial efficiencies of the resulting films were evaluated by the use of both agar plate tests and LB media using *Bacillus subtilis* and *Escherichia coli*. Furthermore, complete leaching and full recharging cycles of Ag^+ ion on the polymer film surfaces were demonstrated.

2. Experimental

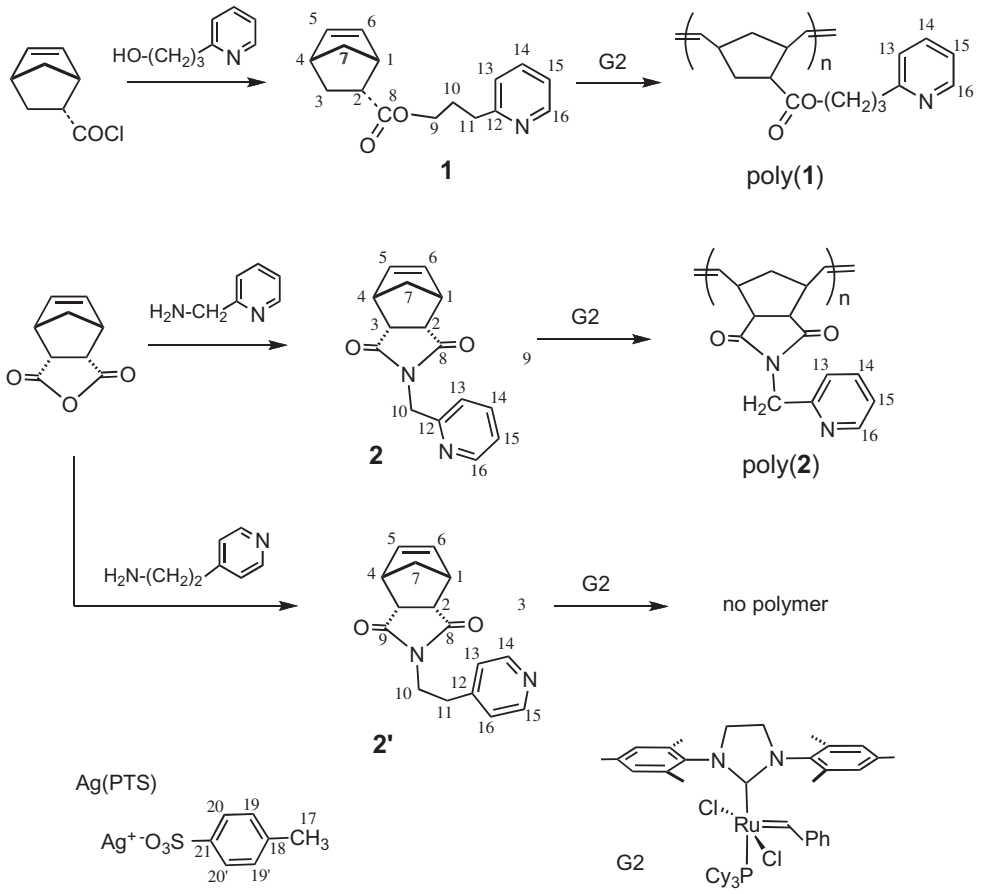
2.1. General procedures and materials

All manipulations that involved air-sensitive compounds were performed under an atmosphere of argon or purified nitrogen using standard Schlenk or dry box techniques. Solvents were dried and deoxygenated by refluxing on sodium or CaH_2 under argon and distilled before use. Grubbs catalyst (G2), 3-(pyridin-2-yl)propan-1-ol, 3-(pyridin-4-yl)propan-1-ol, and 2-(aminomethyl)pyridine were purchased from Sigma–Aldrich Co. and used as received. Dicyclopentadiene, maleic anhydride, and 2-propenoyl chloride were also obtained from Sigma–Aldrich Co. and used to prepare 5-norbornene-*endo*-2.3-dicarboxylic anhydride and 5-norbornene-*endo*-2-carbonyl chloride, respectively, according to the conventional Diels–Alder reaction with cyclopentadiene [17].

^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECA500 spectrometer at 500 and 125.77 MHz, respectively. The NMR signals for monomers and their Ag^+ complexes were fully assigned using DEPT, COSY, HMQC, and HMBC techniques. For the NMR-numbering scheme of the atoms in the monomers, see Scheme 1. IR spectra were recorded on a Jasco FT/IR-4100 spectrometer. The molecular weights of the polymers were measured by TOSOH HLC-8220 GPC using an HZM-H column at 40 °C with THF eluent. Differential scanning calorimetry (DSC) curves were obtained with a SII NanoTechnology DSC-120 cell with an aluminum crucible under a dynamic nitrogen atmosphere. Elemental analyses were performed by Chemical Analysis Team, D & S Center, RIKEN.

2.2. Preparation of norbornene derivative *1*

To a 2-methylpyridine solution (35 ml) of 3-(pyridin-2-yl)propan-1-ol (2.12 g, 15.5 mmol), 5-norbornene-*endo*-2-carbonyl chloride (2.26 g, 14.4 mmol) was added dropwise at 0 °C with stirring. The mixture was stirred at room temperature for 24 h. 2-Methylpyridine was evaporated under reduced pressure. The residue was dissolved in a minimum amount of dichloromethane and chromatographed on a silica-gel column (3 × 20 cm). A yellow band was eluted with dichloromethane followed by a mixture of ethyl acetate and dichloromethane (1:2). The eluate was concentrated almost to dryness under reduced pressure and redissolved in a minimum amount of dichloromethane. The solution was subjected to column chromatography on alumina (3 × 20 cm, deactivated beforehand with 10 wt.% of H_2O). A yellow band, eluted with



Scheme 1. Synthesis of ROMP polymers with a pendant pyridyl group.