



# Synthesis and application of cinnamate-functionalized rubber for the preparation of UV-curable films

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## ABSTRACT

A butyl rubber derivative that can be cured upon exposure to UV light in the absence of additional chemical additives was developed. This polymer was prepared by the reaction of hydroxyl-functionalized butyl rubber with cinnamoyl chloride to provide a cinnamate functionalized rubber. The cinnamate content was varied by starting with derivatives prepared from butyl rubber containing either 2 or 7 mol% isoprene. The kinetics of the cross-linking was studied by UV–visible spectroscopy and it was found to vary according to the film thickness. The changes in gel content and volume swelling ratio with irradiation time were dependent on the cinnamate content. Toxicity studies suggested that the cross-linked materials do not leach toxic molecules. The approach was also applied to obtain cross-linked films of butyl rubber-poly(ethylene oxide) graft copolymers, leading to surfaces that resisted the adhesion and growth of cells. Thus the approach is versatile and is of particular interest when non-leaching coatings of cross-linked butyl rubber are desired for biomedical or other applications.

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## 1. Introduction

Butyl rubber, a copolymer of isobutylene and small percentages of isoprene, is a high performance synthetic elastomer with many attractive properties including high elasticity, impermeability to gas and water, high damping, and good thermal and chemical stability. Because of these properties it is used in a diverse array of commercial applications ranging from automobile tires to sporting equipment. In addition, due to its low toxicity, food grade butyl rubber has been commercialized and is used in a variety of chewing gums.

In the past couple of decades there has also been increasing interest in the development of polyisobutylene (PIB)-based materials for biomedical applications [1–5]. The most noteworthy example has been the clinical use of a PIB-poly-styrene (SIBS) triblock copolymer as a drug eluting coating on the TAXUS<sup>®</sup> vascular stent [3,6]. Similar polymers have also been investigated in corneal shunts for the treatment of glaucoma [7,8], synthetic aortic valves [9], and hydrophobic electrospun fiber mats [10]. PIB-poly(methyl methacrylate) (PMMA) composites have been shown to have enhanced properties relative to commercial bone cements due to the incorporation of the elastomeric PIB into the glassy PMMA material [11,12]. Multiarm PIB-cyanoacrylate (CA) copolymers have been reported as promising materials for intervertebral disk replacement [13,14] and tissue adhesives [15]. PIB-based polyurethanes have been demonstrated to exhibit unprecedented combinations of mechanical properties and high oxidative, hydrolytic and biological stability [4]. Furthermore, copolymers of PIB with

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hydrophilic polymers such as poly(*N,N*-dimethylacrylamide) or poly(ethylene oxide) (PEO) have been used to form membranes that can encapsulate cells while allowing the exchange of oxygen, nutrients, and secreted proteins such as insulin across the membrane [16]. Our group has shown that butyl rubber-PEO films resist the adsorption of proteins and the growth of cells, providing non-fouling properties [17,18]. Butyl rubber-PEO graft copolymers can also assemble into micellar structures in aqueous solution [19].

In traditional, non-biomedical applications, butyl rubber is chemically cross-linked using additives such as zinc oxide or elemental sulfur with additives such as thiuram or thiocarbamates, in order to provide properties such as improved creep resistance, resilience and modulus in comparison to the non-cross-linked rubber. The inclusion of photoinitiators in various formulations of butyl rubber and PIB has provided UV-curable rubbers for applications such as coatings, sealants and adhesives [20–24]. Butyl rubbers that cure with peroxide initiators in the presence of co-agents have also been developed in recent years [25,26]. The above cross-linking processes are not ideal for biomedical applications due to the possibility of leaching toxic additives from the resulting materials. In the case of the SIBS triblock copolymers used in the stent coating applications, the incorporation of the styrene blocks imparts thermoplastic properties to the rubber, allowing the material to behave as a cross-linked rubber at room temperature and melt like plastic at temperatures above the  $T_g$  of polystyrene segments [3]. However, to the best of our knowledge, a butyl rubber derivative that is capable of undergoing chemical cross-linking without the use of chemical additives has not yet been reported.

Cinnamate modified polymers have been demonstrated to undergo cross-linking upon UV irradiation via a [2 + 2] cycloaddition mechanism in the absence of chemical additives such as photoinitiators [27]. For example, Visconte and coworkers prepared cross-linked films of natural rubber by maleation, reaction with various cinnamate derivatives, and then UV treatment [28–30]. The cinnamate-based UV curing approach has also been used for a variety of applications including photopatternable surfaces [31] and also to covalently fix noncovalent polymer assemblies in solution [32,33]. The low toxicity of cinnamic acid makes this a particularly attractive approach for the development of curable butyl rubber films for biomedical application [34]. In addition, the simple preparation of hydroxyl functionalized butyl rubber derivatives recently reported by our group makes the preparation of butyl rubber-cinnamate derivatives a synthetically facile process [17].

We report here the synthesis and chemical characterization of cinnamate functionalized butyl rubber derivatives starting from both low (2 mol%) and high (7 mol%) isoprene content rubbers in order to provide different loadings of cinnamate. The preparation of polymer films is described, followed by studies of their UV curing kinetics, gel content, and swelling ratios. Mammalian cell culture studies demonstrate that toxic molecules do not leach from the cross-linked materials. In addition, it is shown that the approach can be extended to the preparation of cross-linked films of other functional butyl rubber derivatives including butyl rubber-PEO graft copolymers.

## 2. Experimental section

### 2.1. Materials and general procedures

Butyl rubber containing 2 mol% isoprene ( $M_w = 388000$  g/mol, polydispersity index (PDI) = 3.4) and 7 mol% isoprene ( $M_w = 423000$  g/mol, PDI = 2.9) were provided by LANXESS Inc. Polymers **1a**, **1b**, and **2a** were prepared as previously reported [17,19]. Cinnamoyl chloride (Sigma-Aldrich, 96%), reagent grade  $K_2CO_3$ ,  $MgSO_4$  anhydrous were purchased from Caledon and used as received. Reagent grade pyridine (99%, Caledon) was refluxed over  $CaH_2$  for 2 h and distilled prior using.  $^1H$  NMR spectra were obtained at 600 MHz on a Varian INOVA 600 Spectrometer. Chemical shifts are reported in ppm and are calibrated against residual solvent signals of  $CDCl_3$  ( $\delta$  7.26) and coupling constants ( $J$ ) are reported in ppm. Infrared (IR) spectra were obtained using a Bruker Tensor 27 instrument as films from toluene on KBr plates. The UV-visible absorption measurements were performed on a Varian Cary 300 Bio UV-visible spectrophotometer. Size exclusion chromatography was performed in THF with a flow rate of 1 mL/min at 30 °C using a Viscotek GPCmax VE2001 GPC solvent/sample module equipped with a Viscotek VE 3580 differential refractive index detector and two PolyPore (300 mm  $\times$  7.5 mm) columns from Agilent. Molecular weight data is given relative to polystyrene standards. Differential scanning calorimetry (DSC) measurements were acquired under a nitrogen atmosphere with a DSC Q20 calorimeter from TA instruments at heating rate of 10 °C/min from –100 °C to 125 °C, and the reported glass transition temperature were generated from the second of two heating cycles.

### 2.2. Synthesis of polymer **3a**

The hydroxyl functionalized polymer **2a** (1.0 g, 0.39 mmol of hydroxyl) was dissolved in 30 mL of dry toluene and 2 mL pyridine was added, followed by cinnamoyl chloride (0.33 g, 2.0 mmol, 5.0 equiv. per hydroxyl). The reaction was shielded from light with aluminum foil and stirred overnight at room temperature. The resulted polymer was precipitated three times in acetone, then dried under vacuum. Yield: 92%  $^1H$  NMR (600 MHz,  $CDCl_3$ ):  $\delta$  7.71 (d,  $J = 15.8$ , 1H, Ar–CH=), 7.53–7.38 (m, 5H, Ar–H), 6.48 (d,  $J = 15.8$ , 1H, Ar–CH=CH–CO–), 5.32 (br s, 1H, –CH–O–CO–), 5.20 (s, 1H, HC=C, *cis*- to –CH–O–CO–), 4.93 (s, 1H, HC=C, *trans*- to –CH–O–CO–), 1.42 (s,  $CH_2$  polyisobutylene), 1.11 (s,  $CH_3$  polyisobutylene, 78H). IR (thin film,  $cm^{-1}$ ): 2951 (– $CH_3$  stretch), 2918 (– $CH_2$ – stretch), 1718 (–C=O stretch), 1639 (–C=C–C=O stretch), SEC:  $M_w = 355000$  g/mol, PDI = 2.5;  $T_g = -63$  °C.

### 2.3. Synthesis of polymer **3b**

The epoxidized polymer **1b** (1.0 g, 1.2 mmol of epoxide) was dissolved in 30 mL of toluene and 1–2 drops of 10 M HCl was added into the solution. After 3 h, 0.25 g of  $K_2CO_3$  was ground into a fine powder and added to the solution to neutralize excess HCl. The solution turned clear,

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