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## Hyper-branched poly(poly(ethylene glycol)methacrylate)-grafted surfaces by photo-polymerization with iniferter for bioactive interfaces ☆

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#### Abstract

A new hyper-branched surface in which three species of architectures were constructed as stem chain, branched stem and twig chaingrafted branched chain of poly(poly(ethylene glycol)methacrylate) (poly(PEGMA)) by photo-polymerization using dithiocarbamyl group (DC) as iniferter was prepared and characterized. For these surfaces, radical copolymerization of styrene and an iniferter-activated chain that was previously synthesized was performed for using as base materials for surface coating. On a DC-activated surface, hyperbranched poly(PEGMA) was introduced by photo-polymerization and dithiocarbamylation. All modified surfaces were analyzed by Xray photoelectron spectroscopy (XPS) and water contact angle measurements. Our results demonstrated that a highly hyper-branched graft architecture of poly(PEGMA) can be constructed on PU surface by photo-polymerization using dithiocarbamyl group as iniferter, in which first, second and third generation gave stem chain, branched chain and twig chain of poly(PEGMA), respectively. Our hyperbranched surfaces could be regulated by photo-irradiation time and might be controlled by feed amounts or other reaction conditions. This highly dense architecture of PEG chain with hydrophilicity and chain mobility, grafted on surface, is expected to be effectively utilized in bio-implantable substrates or micro- or nano-patterned surfaces for immobilization of bioactive molecules in biomedical fields. © 2008 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Hyper-branched surface; Photo-polymerization; Poly(poly(ethylene glycol)methacrylate) (poly(PEGMA)); Iniferter; Dithiocarbamylation

### 1. Introduction

Many researches have explored strategies to create the biomaterial that can grant new potential functions. Photochemistry is an attractive strategy in the production of such materials because of controlled reaction initiation and termination, an often-short reaction time and spatial control [1–4]. In particular, hyper-branched architectures are very attractive for functional biointerfaces of biomaterials with cells or tissues in biomedical applications [5,6]. Photo-polymerization techniques are useful for preparing hyperbranched architectures. Matsuda and coworkers fabricated

hyper-branched architectures using UV free-radical polymerization [4–9]. Some of the materials with which they have worked include poly(vinyl alcohol) (PVA), poly(ethylene glycol) (PEG), polystyrene (PS), poly(acrylamide) and poly(acrylic acid) (PAA). This type of polymerization with the photo-sensitive dithiocarbamyl group is referred to as a living radical polymerization, or an iniferter polymerization [10]. The iniferter is a compound that acts as an initiator, a transfer agent, and a terminator and the representative iniferter, benzyl N,N-diethyldithiocarbamate, is photolyzed to generate a radical pair (a benzyl radical and an N,N-diethyldithiocarbamyl radical). This iniferter polymerization method, which was first developed for controlled macromolecular architecture in solution by Otsu et al. in the early 1980s [11–14], is particularly beneficial to surface functionalization on fabricated biomedical devices

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[15,16]. With the iniferter-based polymerization, some scientists designed various surface graft architectures controlling the chain length, block graft chain, gradient chain length, and regionally graft-polymerized pattern surface [5,6].

Typically, hydrophillic polymers such as PEG are introduced on surfaces in order to inhibit cell adhesion [3]. This can be further extended by incorporating a hydrophobic copolymer such as polystyrene by photoinitiated copolymerization [17]. The hydrophobic polystyrene allows strong bonding of the copolymer to a poly(ethylene terephthalate) surface, whereas the hydrophilic PEG is highly wettable and cell-adhesion-resistant [3]. PEG is also able to be functionalized with bioactive molecules to promote cell adhesion or growth. Hern et al. showed that peptide derivatized PEG can be photo-polymerized and, depending upon the inclusion of spacer molecules, selective for cell adhesion, as measured by cell spreading [3]. Specifically, PEG without a peptide sequence attached showed little cell spreading, PEG with a peptide attached but without a spacer linkage showed cell spreading nonspecific to the attached peptide sequence, and PEG with a spacer and peptide attached showed cell spreading specific to the peptide sequence [18,19].

In this study, we prepared a hyper-branched surface in which three species of architectures were constructed as stem chain, branched stem and twig chain-grafted branched chain of poly(PEGMA) by photo-polymerization using dithiocarbamyl group (DC) as iniferter. For these surfaces, radical copolymerization of styrene and iniferter-activated chain that was previously an synthesized was performed for using as base materials for surface coating. On a DC-activated surface, hyperbranched poly(PEGMA) was introduced by photopolymerization and dithiocarbamylation. All modified surfaces were analyzed by X-ray photoelectron spectroscopy (XPS) and water contact angle measurements. This type of hyper-branched surface is expected to be applied to many kinds of biomaterials.

#### 2. Experimental

#### 2.1. Materials

Vinylbenzyl chloride (VBC, *m* and *p* mixture) and styrene (ST) were purchased from Aldrich Chemical Co. and used after further conventional purification containing distillation. Sodium *N*, *N*-diethyldithiocarbamate trihydrate (NaDC, Aldrich Chemical Co.) was used as received without further purification. Poly(ethylene glycol)methacrylate (PEGMA,  $M_n = 360$ ) was provided from Aldrich Chemical Co. All other reagent grade chemicals and solvents were used as received without further purification. Polyurethane (PU) film was used as substrates.

#### 2.2. Synthesis of photoreactive monomer (VBDC)

A photo-reactive monomer, vinylbenzyl N,N-diethyldithiocarbamate (VBDC), was prepared from vinylbenzyl chloride and sodium N,N-diethyldithiocarbamate as shown in Scheme 1. Sodium N,N-diethyl dithiocarbamyl trihydrate (NaDC) (10 g, 0.044 mol) and ethanol (40 ml) were placed in a 250 ml three-necked flask with a stirrer, a dropping funnel, and a reflux condenser. To this solution 8 ml of ethanol solution of VBC (5 g, 0.033 mol) was added at 0 °C. The solution was stirred for 24 h at room temperature. Then the reaction mixture was poured into a large amount of water and extracted with ether. The organic phase was washed with water, dried (Na<sub>2</sub>SO<sub>4</sub>), filtered, and evaporated under vacuum. The residue was recrystallized three times from methanol. The yield of synthesized VBDC was 33.5%.

#### 2.3. Synthesis of poly(ST-VBDC)

Poly(ST–VBDC) was prepared by radical copolymerization of VBDC and ST as previous reports (Scheme 1) [4]. A glass flask containing a mixture of ST (2.29 ml, 0.02 mol), VBDC (*m* and *p* mixture, 1.325 g, 0.005 mol),



Scheme 1. Synthetic route of VBDC and poly(ST-VBDC).

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