DENTAL MATERIALS 23 (2007) 395–403

available at www.sciencedirect.com

ScienceDirect

journal homepage: www.intl.elsevierhealth.com/journals/dema

Synthesis and preparation of novel 4-arm star-shape poly(carboxylic acid)s for improved light-cured glass-ionomer cements

Dong Xie, Jong-Gu Park, Jun Zhao*

Department of Biomedical Engineering, Purdue School of Engineering and Technology, Indiana University-Purdue University at Indianapolis, Indianapolis, IN 46202, USA

ARTICLE INFO

Article history:
Received 7 December 2005
Received in revised form
13 January 2006
Accepted 3 February 2006

Keywords:
4-Arm star-shape poly(acrylic acid)
ATRP
Light-cured glass-ionomer cement
Synthesis
Tethering
Compressive properties

ABSTRACT

Objective. The objective of this study was to synthesize and characterize novel 4-arm star-shape poly(acrylic acid)s (poly(AA)s) via atom-transfer radical polymerization (ATRP) technique, tether in situ light-curable methacrylate functionalities onto the poly(AA) backbone, use these star-shape poly(AA)s to formulate the light-cured glass-ionomer cements (LCGICs), and evaluate the mechanical strengths of the formed cements.

Materials and methods. The 4-arm poly(AA)s were synthesized using ATRP and tethered with either 2-isocyanatoethyl methacrylate (IEM) or glycidyl methacrylate (GM). The polymers were formulated with 2-hydroxyethyl methacrylte (HEMA) or methacryloyl beta-alanine (MBA), water, initiators, and Fuji II LC filler. Compressive strength (CS) was used as a tool to evaluate the formed cements. The specimens were conditioned in distilled water at 37 °C for 24 h prior to testing.

Results. The 4-arm poly(AA) showed a lower viscosity as compared to its linear counterpart. Both IEM-tethered and GM-tethered 4-arm poly(AA) constructed LCGICs showed significantly high mechanical strengths. Both types of co-monomer and grafting agent dramatically affected the mechanical strengths. The MBA-containing poly(AA) cements exhibited much higher CS than the HEMA-containing cements. The IEM-tethered poly(AA) cements showed much higher CS and DTS than the GM-tethered cements.

Conclusions. This study developed a novel light-curable 4-arm star-shape poly(AA) system. The system was 13% in CS, 178% in DTS and 123% in FS, compared to Fuji II LC.

1. Introduction

Glass-ionomer cements are one of the most promising restoratives in dentistry [1]. Since their invention, these cements have been successfully applied in dentistry for more than 25 years [1–4]. The success of these cements is attributed to the facts that they are known for their unique properties such as direct adhesion to tooth structure and base metals [5,6], anticariogenic properties due to release of fluoride [7], thermal compatibility with tooth enamel and dentin because of low coefficients of thermal expansion similar to that of tooth structure [8], minimized microleakage at the tooth-enamel interface due to low shrinkage [8], and low cytotoxicity [9,10].

An acid–base reaction between calcium and/or aluminum cations released from a reactive glass and carboxyl anions pendent on polyacid describes the setting and adhesion mechanism of GICs [2,11]. The polymer backbones of GICs have been made by poly(acrylic acid) homopolymer, poly(acrylic

* *Corresponding author*. Tel.: +1 317 274 9748; fax: +1 317 278 2032.
E-mail address: dxie@iupui.edu (D. Xie).

0109-5641/$ – see front matter © 2006 Academy of Dental Materials. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.dental.2006.02.008

acid-co-itaconic acid) or/and poly(acrylic acid-co-maleic acid) copolymers [1,2,11]. These GICs are called conventional glass-ionomer cements (CGICs) or self-cured GICs [1–4]. Despite numerous advantages of CGICs, brittleness, low tensile and flexural strengths have limited the current CGICs for use only at certain low stress-bearing sites such as Class III and Class V cavities [1,2]. Much effort has been made to improve the mechanical strengths of CGICs [1,4,11] and the focus has been mainly on improvement of polymer backbone or matrix [1,4,11,12–18]. Briefly two main strategies have been applied. One is to incorporate hydrophobic pendent (meth)acrylate moieties onto the polyacid backbone in CGIC to make it become light- or redox-initiated resin-modified GIC (RMGIC) [12–15,17] and the other is to directly increase molecular weight (MW) of the polyacid [16–18]. As a result, the former has shown significantly improved tensile and flexural strengths as well as handling properties [12–15,17]. The strategy of increasing MW of the polyacid by either introducing amino acid derivatives or *N*-vinylpyrrolidone has also shown enhanced mechanical strengths [16–18]; however, the working properties were somehow decreased because strong chain entanglements formed in these high MW linear polyacids resulted in an increased solution viscosity [16,17]. So far, all the polyacids used in the GIC formulations have been linear polymers and are synthesized via conventional free-radical polymerization.

It has been noticed that polymers with star, hyperbranched or dendritic shapes often demonstrate low solution or melt viscosity because these molecular structures behave similar to a solution of hard spheres and exhibit limited chain entanglements, which is beneficial to polymer processing [19,20]. Therefore, we hypothesized that it might be possible to increase MW without or with less viscosity increase if the polyacids in current CGICs were star-shaped (or spherical) or dendritic. As we know, however, it is absolutely impossible to make star-shaped polyacids by using current conventional free-radical polymerization techniques. Nevertheless, the most recent development of living free-radical polymerization technologies such as atom-transfer radical polymerization (ATRP) [21] may well help us to test our proposed hypothesis.

This article reports the synthesis and characterization of novel 4-arm star-shape poly(acrylic acid)s via ATRP technique, tether in situ light-curable methacrylate functionality onto the polyacid backbone, use of these light-curable star-shaped poly(acrylic acid)s to formulate the cements with glass fillers, and evaluation of the mechanical strengths of the formed cements.

2. Materials and methods

2.1. Materials

Pentaerythritol, triethylamine (TEA), 2-bromoisobutyryl bromide (BIBB), CuBr, *N*,*N*′*N*′*N*′*N*″-pentamethyldiethylenetriamine (PMDETA), dl-camphoroquinone (CQ), diphenyliodonium chloride (DC), 2,2′-azobisisobutyronitrile (AIBN), dibutyltin dlaurate (DBTL), triphenylstibine (TPS), pyridine, *tert*-butyl acrylate (*t*-BA), methacryloyl chloride, beta-alanine (BA), 2-hydroxyethyl methacrylate (HEMA), 2-isocyanatoethyl methacrylate (IEM), glycidyl methacrylate (GM), anhydrous magnesium sulfate ($MgSO_4$), sodium hydroxide (NaOH), hydrochloric acid (HCl, 37%), diethyl ether, tetrahydrofuran (THF), methanol (MeOH), deuterated methyl sulfoxide, and ethyl acetate were used as received from VWR International Inc. (Bristol, CT) without further purifications. GC Fuji II™ and GC Fuji II™ LC glass powders were supplied by GC America Inc. (Alsip, IL).

2.2. Synthesis and characterization

2.2.1. Synthesis of the 4-arm pentaerythritol tetrakis(2-bromoisobutyrate) initiator

The 4-arm initiator was synthesized following the procedures described by Wang et al., with a slight modification [22]. Briefly, to a reactor charged with 100 ml (0.72 mole) of TEA, 15 g (0.11 mole) of pentaerythritol and 200 ml of THF, a mixture of 100 ml (0.81 mole) of BIBB in 25 ml of THF was added drop-wise with stirring at room temperature. After addition was completed, additional 1 h was added to complete the reaction. The solution was washed with 5% NaOH and 1% HCl and then extracted with ethyl acetate. The extract was dried with anhydrous $MgSO_4$, concentrated in vacuo and crystallized. The final product was re-crystallized from diethyl ether. The schematic diagram for the 4-arm initiator synthesis is shown in Fig. 1(a).

2.2.2. Synthesis of the 4-arm poly(acrylic acid) via ATRP

To a flask containing dioxane (5.0 g or 0.056 mole), 4-arm initiator (1% by mole), PMDETA (3%, ligand) and *t*-BA (5.0 g or 0.04 mole) were charged. The CuBr (3%) was incorporated under N_2 purging after the above solution was degassed and nitrogen-purged by three freeze–thaw cycles. The solution was then heated to 120 °C to initiate the ATRP [23]. FT-IR was used to monitor the reaction. After the polymerization was completed, the poly(*t*-BA) polymer was precipitated from water. CuBr and PMDETA were removed by re-precipitated from dioxane/water. The colorless polymer was then hydrolyzed in a mixed solvent of dioxane and HCl (37%) [24] (dioxane/HCl = 1/3) under refluxed condition for 6–18 h, depending on the molecular weight of the polymer. The hydrolyzed poly(acrylic acid) was dialyzed against water until the pH in water became neutral. The purified 4-arm poly(acrylic acid) (poly(AA)) was obtained after freeze-dried. The reaction scheme for poly(AA) synthesis via ATRP is described in Fig. 1(a). Three 4-arm poly(AA) polymers with the same feed *t*-BA were synthesized at the initiator concentration of 0.5, 1.0 and 1.5%, respectively.

2.2.3. Synthesis of the IEM-tethered 4-arm poly(AA)

IEM-tethered poly(AA) was synthesized as described elsewhere [17]. Briefly, to a three-neck flask containing poly(AA) (4.1 g or 0.057 mole), THF (18 ml), BHT (0.1%, by weight), TPS (0.1%) and DBTL (2%), a mixture of IEM (3.1 g or 0.02 mole for 35% grafting or 4.4 g or 0.029 mole for 50% grafting) and 3.7 ml of THF was added drop-wise at 40 °C under a nitrogen blanket. Fourier transform-infrared (FT-IR) spectroscopy was used to monitor the reaction. The polymer tethered with IEM was recovered by precipitation from diethyl ether, followed by dry-