# Preparation of Photo-curable 3-Arm Star-shape Polyacid-based Glass-ionomers via Aqueous ATRP

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*Abstract*—A photo-curable 3-arm star-shape polyacrylic acid was synthesized via aqueous atom-transfer radical polymerization (ATRP), followed by tethering with 2-isocyanatoethyl methacrylate. The purified polymer was used to formulate with water, comonomer and Fuji II LC filler to form a photocurable glass-ionomer cement. Compressive strength (CS) was used for evaluation. The effects of MW, comonomer, filler powder/polymer liquid (P/L) ratio and aging on CS were investigated. All the specimens were conditioned in distilled water at 37 $^{\circ}$C for 24 h prior to testing. Although the ATRP reaction was run at room temperature in the presence of water, it was extremely fast with significant exotherm generation and the 90 % conversion was achieved only at 10 min. The effects of MW and comonomer on CS were significant. It was found that the MBA-containing cement exhibited much higher CS than the HEMA-containing cement due to salt-bridge contribution of the MBA. Increasing P/L ratio increased CS. In the course of aging, the novel cement showed a continuous increase in yield strength, ultimate strength and modulus in compression within 30 days, indicating that a salt-bridge formation is a gradual process for this system.

*Keywords*—*antibacterial 3-Arm star-shape polyacrylic acid; aqueous ATRP synthesis; glass-ionomer cement; compressive strength*

## I. INTRODUCTION

Glass-ionomer cements (GICs) are known to be one of the most promising materials among current dental restoratives [1]. Since their invention, these cements have been successfully applied in dentistry for more than 30 years [1-4]. The success of these cements is attributed to the facts that they have very 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].

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

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]. So far, all the polyacids used in the GIC formulations have been linear polymers and are synthesized via conventional free-radical polymerization. If the polyacids could be made with star or hyperbranched shapes, the concept of using high MW polymer to increase mechanical strengths might be workable because the increased viscosity by MW might be offset by the reduced viscosity provided by star or hyperbranched polyacids. That is our hypothesis. 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.

Atom transfer radical polymerization (ATRP) proves to be an effective method to assemble polymers with well controlled molecular weight and well defined molecular architectures [21], as compared to anionic or cationic polymerization. ATRP has been predominantly studied in homogeneous organic systems, i.e. bulk or solution polymerizations [21]. With the rapid development of understanding of these controlled systems, one of the biggest challenges is to extend the application of ATRP methods to aqueous media. Indeed, polymerizations being carried out in aqueous media are receiving more and more attention because water is abundant and safe to the environment. In contrast to the numerous controlled polymerization methods employed in organic media, aqueous polymerization is mainly focused on radical polymerization, since it is impossible to conduct essentially any ionic polymerization in water. Both increased environmental concerns and the rapid growth of pharmaceutical and biomedical applications for hydrophilic polymers require water as the necessary reaction medium. In the case of biomedical applications, synthesis in aqueous media has additional importance because almost all the organic solvents are cytotoxic to cells and tissues unless they are 100% removed. It is known that most cytotoxicities are caused by leached small organic molecules, including unreacted monomers and extractable organic solvents [22, 23]. The examples of the polymers synthesized in water via ATRP include linear poly (2-hydroxyethyl methacrylate) [24], linaer poly(ethylene glycol) [25] and linear poly(methacrylic acid) [26]. Polymers based on acrylic acid have become increasingly important in applications for coatings and biomaterials. However, acrylic acid and methacrylic acid are difficult to directly polymerize via ATRP because of interactions of the carboxylic acid functionalities with the catalyst [27]. Presumably, carboxylic acids react with Cu ions by displacing the halogen atom, resulting in the formation of metal carboxylates that inhibit deactivation. Additionally, since many of the ligand systems utilized in ATRP are nitrogen based, protonation of the nitrogen may occur, disrupting its coordination to the Cu center. Therefore, these acid monomers have to be protected before they undergo ATRP. Recent reports showed that the protection could be executed by formation of inorganic salts [27, 28]. Synthesis of poly(carboxylic acid) in aqueous ATRP are still in embryonic stages and so far only a couple of reports regarding synthesis of linear poly(methacrylic acid) and poly(acryloyl beta-alanine) have been published [26, 28].

The objective of this study was to synthesize and characterize 3-arm star-shape polyacrylic acid in aqueous solution via atom-transfer radical polymerization technique, to tether *in situ* light-curable methacrylate functionality onto the polyacid backbone, to use these synthesized polymers to formulate the cements with glass fillers, and to evaluate the compressive strengths of the formed cements.

## II. MATERIAL AND METHODS

### A. Materials

Tris(hydroxymethyl)aminomethane (THMAM), triethylamine (TEA), trimellitic anhydride (TMA), 2-bromopropionyl bromide (BPB), CuBr, N,N,N'N'N'’-pentamethyldiethylenetriamine (PMDETA), dl-camphoroquinone (CQ), diphenyliodonium chloride (DC), 2,2'- azobisisobutyronitrile (AIBN), dibutyltin dlaurate (DBTL), triphenylstibine (TPS), acrylic acid (AA), methacryloyl chloride, beta-alanine (BA), 2-hydroxyethyl methacrylate (HEMA), 2-isocyanatoethyl methacrylate (IEM), anhydrous magnesium sulfate ($MgSO_4$), sodium hydroxide (NaOH), hydrochloric acid (HCl, 37%), ethylenediaminetetraacetic acid (EDTA), diethyl ether, tetrahydrofuran (THF), methanol (MeOH), N-methylpyrrolidone (NMP), deuterated methyl sulfoxide, and ethyl acetate were used as received from VWR International Inc (Bristol, CT) without further purifications. GC Fuji II[TM] LC glass powder was supplied by GC America Inc (Alsip, IL).

### B. Synthesis and Characyterization

*1) Synthesis of the 3-Arm THMAM-TMA-BPB Initiator:* The 3-arm THMAM-TMA-BPB initiator was synthesized based on the following two steps: synthesis of THMAM-TMA and synthesis of 3-arm THMAM-TMA-BPB. Briefly, to a reactor charged with 200 ml MeOH, 47.5 g (0.25 mole) of TMA and 30g (0.25 mole) of THMAM were added at room temperature. After 2 h reaction, the solvent was completely removed in vacuo and the product THMAM-TMA was used for synthesis of THMAM-TMA-BPB. To a reactor charged with THMAM-TMA (10 g, 0.032 mole), TEA (9.7 g, 0.096 mole) and NMP (80 ml), BPB was added dropwise at 5-10 $^oC$ with stirring. After reaction for 3 h, the solution was filtered, washed with distilled water and extracted with ethyl acetate. The extract was dried with anhydrous $MgSO_4$, concentrated in vacuo, and finally stored in a vacuum oven. The schematic diagram for the 3-arm initiator synthesis is shown in Fig.1.

*2) Synthesis of the 3-Arm Poly(acrylic acid) via Aqueous ATRP:* To a flask containing water (50.0 g), MeOH (8.3 g), AA (13.07g or 0.186 mole) and NaOH (7.442 g or 0.201 mole), 3-arm initiator (1% by mole) and PMDETA (3%, ligand) were charged. The CuBr (3%, catalyst) was incorporated under $N_2$ purging after the above solution was degassed and nitrogen-purged by three freeze-thaw cycles. The high exotherm was observed and recoreded right after the CuBr was added. ^{1}HNMR was used to monitor the conversion of

the monomers. After 2 h reaction, the blue color sodium salts of poly(acrylic acid) (PAA) were mixed with EDTA (0.37 mole) and acidified with HCl (37%) until pH = 2.0. The obtained mixture was dialyzed against water until the pH in water became neutral. $Cu^+$, $Cu^{2+}$ and PMDETA were removed by EDTA and dialysis, since the Cu-EDTA complex and PMDETA are water-soluble. The purified colorless 3-arm PAA was obtained after freeze-dried. The reaction scheme for the 3-arm PAA synthesis via ATRP is also described in Fig.1. Three 3-arm PAA polymers with the same feed AA were synthesized at the initiator concentration of 1.0, 2.0 and 3.0%, respectively.
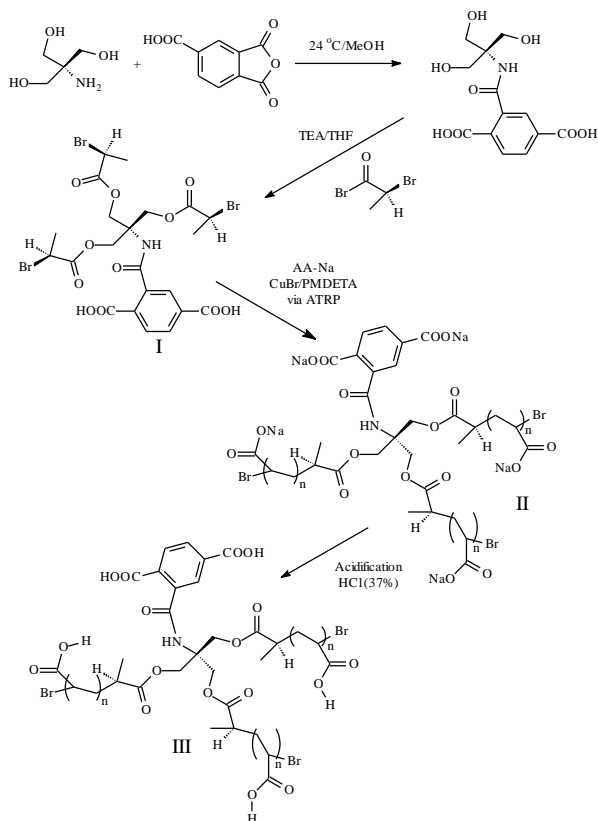


*Fig. 1. Schematic diagram for synthesis: (a) synthesis of the 3-arm BPB initiator; (b) synthesis of the 3-arm PAA via ATRP; (c) Tethering either IEM onto the 3-arm PAA.*

*3) Synthesis of the IEM-tethered 3-Arm PAA:* IEM-tethered PAA was synthesized as described elsewhere [17]. Briefly, to a three-neck flask containing PAA (4.1g 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 dropwise at 40 $^o$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 drying in a vacuum oven at 23 $^o$C. The scheme for synthesis of the IEM-tethered PAA is described in Fig.1.

*4) Synthesis of the MBA:* Methacryloyl beta-alanine (MBA) was synthesized following our previous publication [29]. Briefly, to a reactor containing beta-alanine (BA) and NaOH (NaOH/BA = 2:1, by mole) aqueous solution, methacryloyl chloride equivalent to BA (by mole) was added at 5 $^o$C. After completion of the reaction, the solution was acidified to pH = 2 with HCl (37%) and extracted three times with ethyl acetate. The extract was dried with anhydrous $MgSO_4$ and concentrated using a rotary evaporator to obtain white crystals.

*5) Characterization of the Initiator and Polymers:* The synthesized 3-arm initiator was characterized by Fourier transform-infrared (FT-IR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy. The 3-arm PAA and IEM-tethered PAA were identified by FT-IR and NMR spectroscopy. FT-IR spectra were obtained on a FT-IR spectrometer (Mattson Research Series FT/IR 1000, Madison, WI). $^1$H NMR spectra were obtained on an ARX-300 NMR Spectrometer using deuterated methyl sulfoxide (DMSO) as a solvent. The molecular weights of PAA polymers were determined from $^1$H NMR spectra.
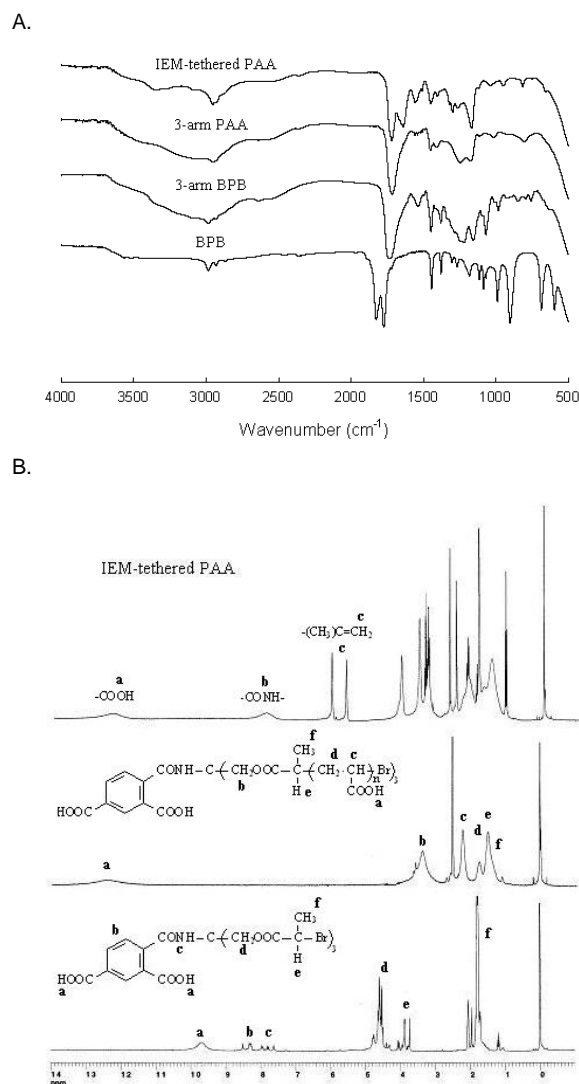
A.



B.



*Fig. 2. FT-IR and $^1$HNMR spectra: (A) FT-IR: BPB, 3-arm BPB initiator, 3-arm PAA, and IEM-tethered 3-arm PAA; (B) $^1$HNMR: 3-arm BPB initiator, 3-arm PAA, and IEM-tethered 3-arm PAA.*

The chemical structures of the synthesized polymer and its precursors were characterized by Fourier transform-infrared (FT-IR) spectroscopy. The formed polymer was characterized by gel permeation chromatography (GPC). FT-IR spectra were obtained on a FT-IR spectrometer (Mattson Research Series FT/IR 1000, Madison, WI). For determination of molecular weight, the polymer was treated with diazomethane, which was generated from diazald reacted with potassium hydroxide (KOH) in water/ethanol solution at 65 $^{o}$C, to obtain partially esterified products [29], having solubility in THF for molecular weight estimation. Molecular weight was estimated on a Waters GPC unit (Model 410 differential refractometer, Waters Inc., Milford, MA) with THF as a solvent, using standard GPC techniques and polystyrene standards.

### C. Evaluation

The experimental cements were formulated with a two-component system (liquid and powder) [17]. The liquid was formulated with IEM-tethered polyacrylic acid, water, 0.7% CQ (photo-initiator, by weight), 1.4% DC (activator) and 0.05% HQ (stabilizer). Fuji II LC kit with a P/L ratio of 3.2 (recommended by manufacturer) was used as control. Specimens were fabricated at room temperature according to the published protocol [16, 17]. Briefly, the cylindrical specimens were prepared in glass tubing with dimensions of 4 mm diameter x 8 mm length. Specimens were removed from the mold after 15 min in 100% humidity, and conditioned in distilled water at 37 $^{o}$C for 24 h. Light-cured specimens were exposed to blue light (EXAKT 520 Blue Light Polymerization Unit, 9W/71, GmbH, Germany) for 1 min before conditioned in 100% humidity. Testing of specimens was performed on a screw-driven mechanical tester (QTest QT/10, MTS Systems Corp., Eden Prairie, MN), with a crosshead speed of 1 mm/min. The sample sizes were n = 6-8 for each group. CS was calculated using an equation of CS = $P/\pi r^2$, where P = the load at fracture and r = the radius of the cylinder. One-way analysis of variance (ANOVA) with the *post hoc* Tukey-Kramer multiple range test was used to determine significant differences of strengths among the materials in each group. A level of α = 0.05 was used for statistical significance.

### III. RESULTS AND DISCUSSION

#### A. Characterization

Fig. 2 shows the spectra for BPB, 3-arm BPB, 3-arm PAA and IEM-tethered PAA. The characteristic peaks are listed below: (1) BPB (cm$^{-1}$): carbonyl: 1826 and 1777 (C=O stretching, strong) and 944 (C=O bending); C-Br: 902, 687 and 595 (C-Br bending); CH$_3$: 1444, 1378 and 1114 (CH$_3$ bending) and 2983-2930 (weak C-H stretching). (2) 3-arm BPB: carbonyl: 1734 (carbonyl and amide I, strong) and 1539 (amide II); C-Br: 1156 and 846 (C-Br bending); C-O: 1220 and 1156 (C-O stretching); CH$_3$: 1447, 1380, 1070 and 984 (CH$_3$ bending); 846, 800 and 758 (C-H

stretching on phenyl ring, weak); and 3690-2200 (COOH, broad). (3) 3-arm PAA: carbonyl: 1716 (C=O stretching, strong); C-O-C: 1245 and 1172 (C-O stretching); and 1406, 1016 and 802 (CH$_3$ bending). (4) IEM-tethered PAA: carbonyl: 1718 (C=O stretching on COO and CONH, where both carbonyl peaks were overlapped); C=C: 1637 (C=C bending); 1557 (amide II, CONH); C-O-C: 1168 (C-O stretching); CH$_3$: 1449, 1405, 1299, 1037 and 816 (CH$_3$ bending); 949 (C=O bending); and 3696-2300 (COOH, broad). The significant shift of carbonyl group from two peaks at 1826 and 1777 to one peak at 1734 and disappearances of 944 strongly confirmed the formation of the 3-arm BPB. The peak at 1637 identified the difference between the 3-arm PAA and IEM-tethered 3-arm PAA.

Fig. 2 also shows the $^1$HNMR spectra for the 3-arm BPB, 3-arm PAA and IEM-tethered 3-arm PAA. The chemical shifts of the 3-arm BPB initiator were found as follows (ppm): a: 9.7 (COOH); b: 8.3 (CONH); c: 7.7-8.0 (CH); d: 4.75 (CH$_2$); e: 3.85 and f: 1.95 (CH$_3$). The chemical shifts of the 3-arm PAA were listed below (ppm): a: 12.3 (COOH); b: 3.4 (CH$_2$); c: 2.25 (CH); d: 1.8 (CH$_2$); e: 1.65 (CH) and f: 1.1 (CH$_3$). The single peak at 2.50 (between b and c) was the chemical shift for solvent DMSO. The typical chemical shifts for the IEM-tethered 3-arm PAA were shown below (ppm): a: 12.15 (COOH), b: 7.9 (CONH), and c: 6.15 and 5.75 (C=CH$_2$). The characteristic chemical shifts at 7.9 as well as 5.75 and 6.15 identified the difference between 3-arm PAA and IEM-tethered 3-arm PAA.

#### B. Synthesis

Synthesis of the 3-arm PAA Atom-transfer radical polymerization (ATRP), a recently developed technology for controlled radical polymerization, is capable of making various architectures such as star polymers, graft copolymers and block copolymers [21]. As we know, almost all the poly(carboxylic acid)s being used in current dental GICs are linear polymers and synthesized via conventional free radical polymerization. So far no reports have been found on studies of different architectures of the polyacids for GIC applications. One of the main reasons may be attributed to the fact that it is impossible to synthesize the polymers with different architectures by using conventional free-radical polymerization techniques. By using ATRP technique, one will be able to synthesize PAA with different architectures. It is known that current poly(carboxylic acid)s are synthesized either in water [2, 4] or in organic solvent such as THF [12, 17] or DMF [14]. Water is often a preferred solvent because of environmental and cytotoxicity concerns. However, synthesis in aqueous media is always a challenging issue because most chemicals can react with water. In this study, we have successfully synthesized the 3-arm star-shape PAA using water as a reaction medium. Since no water-soluble 3-arm initiators are available and no one has ever reported synthesis of the 3-arm PAA in aqueous medium, two barriers have been overcome during the

study: (1) synthesis of water-soluble or partially water-soluble 3-arm initiators and (2) synthesis of the 3-arm PAA in aqueous medium. The initiator precursor we synthesized was THMAM-TMA containing two carboxylic acids, as shown in Fig. 1. Due to introduction of these two carboxylic acid functionalities, the initiator was able to form the sodium salts when pH = 8-9 and thus the synthesized 3-arm BPB initiator was able to dissolve in slightly basic aqueous medium since aqueous ATRP requires the aqueous medium to be slightly basic to avoid protonation of the ligand [30].

TABLE I.    CHARACTERIZATION OF SYNTHESISED PAAs

| [I] (by mole)[1] | 1% | 2% | 3% |
|---|---|---|---|
| Conversion (%)[2] | 97.0 | 98.7 | 99.0 |
| MW (Dalton)[3] | 7,708 | 4,274 | 3,096 |
| MW (Dalton)[4] | 7,924 | 4,321 | 3,120 |
| Temperature ($^{o}$C)[5] | 33.1 | 36.1 | 33.9 |

[1][I] = 3-arm BPB initiator concentration; [2]Conversion was determined from ^{1}HNMR spectrum at reaction time = 2 h; [3]MW was determined from ^{1}HNMR spectrum; [4]MW = calculated theoretical MW; [5]Temperature change was measured *in situ* during ATRP reactions.
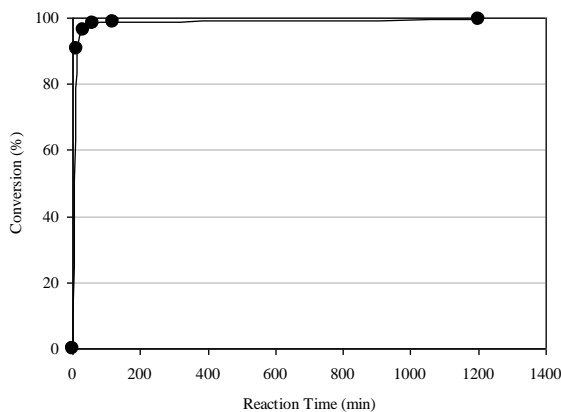


Fig. 3. Conversion of AA vs. time: Conversion of AA monomer was determined from ^{1}HNMR. The 3-arm PAA was prepared in water at pH = 8.0 via ATRP in the presence of the 3-arm BPB, CuBr and PMDETA.

Table I shows the conversion, MW and peak reaction temperature change of the three 3-arm PAAs. The MWs of the 3-arm PAAs synthesized via ATRP were 7,708, 4,274, and 3,096 Daltons, which were determined by ^{1}HNMR and were consistent with the MWs calculated theoretically. The conversions of the monomer to polymer were determined using FT-IR spectra and they were all greater than 97% at 2 h. Fig. 3 exhibits the in situ conversion curve of the PAA with MW of 4,274. Apparently the conversions reached 90.6%, 96.3%, 98.5%, 98.7% and 99.5% at 10 min, 30 min, 60 min, and 102 min (2 h), respectively, which indicates that the reaction is highly efficient as compared to conventional free-radical polymerization [2, 18]. Such fast reactions were also demonstrated by significant temperature changes. As shown in Table I and Fig. 4, the peak temperature changes ($^{o}$C) for all the polymers synthesized in this study were very significant, ranging from 33.1 to 36.1, indicating that

the polymerizations are very exothermic. The results indicate that this aqueous ATRP synthesis of 3-arm PAA is a very efficient and environmental friendly reaction.
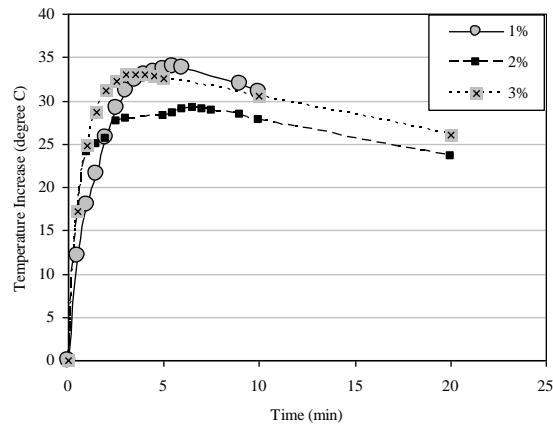


Fig. 4. Temperature increase vs. time: A temperature increase (exotherm) was measured in situ using a digital thermometer during the ATRP reactions. Three 3-arm PAA polymers were synthesized at the initiator concentration of 1%, 2% and 3%, respectively.

*C.    Evaluation*

*1) Effects of MW and Comonomer on CS:* Light-cured glass-ionomer cements (LCGICs) are more attractive dental restorative materials as compared to conventional GICs, due to their significantly high mechanical strengths and easy manipulated working properties [4]. In this study, we used newly synthesized IEM-tethered 3-arm star-shape polyacrylic acids to formulate the GICs with comonomers (HEMA or MBA), water and Fuji II LC glass fillers. First, we examined the effects of both MW of PAA and comonomer on compressive strength. YS (yield strength), CS (ultimate compressive strength) and M (modulus) were used as tools to evaluate the CS, as shown in Table II. Codes A, C, and E stand for the cements synthesized with 1%, 2% and 3% initiators and mixed with MBA, whereas B, D and F represent the cements synthesized with 1%, 2% and 3% initiators and mixed with HEMA. By comparing A, C and E, the cement synthesized with a lower initiator concentration showed higher mechanical strengths, indicating that the higher MW the higher the mechanical strength. The strengths were in decreasing order: A (91.3 MPa in YS, 183.6 MPa in CS and 4.01 GPa in M) > C (79.4, 187.9 and 3.68) > E (62.1, 155.5 and 3.07). The similar trend was also observed for HEMA-based cements. We have also noticed that the cements synthesized using 2% initiators seems the highest in CS for either MBA or HEMA-based cements, which may be attributed to lower solution viscosity in the 2% initiator-containing cements as compared to 1% initiator-containing cements. The effect of comonomer was very significant. By comparing A and B, C and D, and E and F, it is apparent that 78%, 105% and 112%

increase in YS, 23%, 21% and 22% increase in CS, and 151%, 102% and 98% increase in M were observed when MBA replaced HEMA in the cements. This can be attributed to salt-bridge formations contributed by MBA, because salt-bridges often make the cements more brittle [2, 3] and brittle materials are high in CS. In addition, the hydroxyl groups do not make contributions to strength improvement, theoretically speaking. That is why the MBA-containing cements were significantly higher in YS, CS and M than the HEMA-containing cements.

*2) Effect of Glass Powder/Polymer Liquid Ratio on Compressive Strength:* The glass powder/polymer liquid (P/L) ratio is one of the most important parameters in formulating GICs [2, 4]. A higher P/L ratio usually results in higher mechanical strengths, especially CS [31, 32], but it also shortens working time [2]. Since working time is not a problem for a light-curable GIC system, a higher P/L ratio is used in LCGICs, such as Fuji II LC (3.2). We investigated the effect of three P/L ratios (2.2, 2.7, 3.0 and 3.2) on CS and the results are shown in Fig. 5. A significant increase in CS (2.2: 147.1 $\pm$ 11MPa; 2.7: 187.9 $\pm$ 7; 3.0: 215.3 $\pm$ 7.5; and 3.2: 231.0 $\pm$ 2.0) was observed when the P/L ratio was increased. No statistical difference was found between 3.0 and 3.2, which can be attributed to inconsistent mixing because we did experience a difficult mixing at P/L ratio = 3.2.
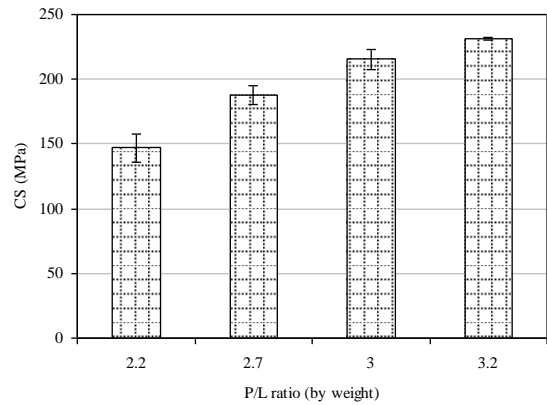


*Fig. 5. Effect of glass powder/polymer liquid (P/L) ratio on CS: MW of the 3-arm PAA = 4,274 Daltons; Filler = Fuji II LC; Grafting ratio of IEM = 50% (by mole); polymer/MBA/water = 50:25:25 (by weight). Specimens were conditioned in distilled water at 37 °C for 24 h.*

*3) Effect of Initiator Concentration a Aging in water:* It is known that GICs increase their strengths with time due to constant salt-bridge formations [3]. In order to examine the effect of the newly synthesized star-shape PAA-composed GIC on compressive strengths during aging, the 50% IEM-tethered 3-arm PAA-composed cement mixed with MBA, and water and glass fillers at P/L = 3.0 was conditioned at 37 °C in distilled water for 1 h, 1day, 3 days and 7 days, 14 days and 30 days, followed by compressive strength determinations. The fractured specimens at each sampling internal were freeze-dried and analyzed using FT-IR spectroscopy. As shown in Fig. 6, the compressive strengths were significantly increased from 21.4 to 171.7 MPa in YS, 145.0 to 284.1 MPa in CS, and 1.3 to 6.7 GPa in M within 30 days (1 month). This result is somehow different from those published previously for linear polycarboxylic acid-based cements in which the strengths of the cements often reach a plateau within 7 days [33]. One of our previous studies regarding linear polycarboxylic acid-containing cements showed that the CS had almost no change after 1 day-aging in water (197.8 MPa at 1 h, 259 MPa at 24 h, 254 MPa at 1 week, 264 MPa at 1 month and 262 MPa) [33]. This interesting phenomenon may be attributed to the spherical nature of these novel star-shape polymers in that the salt-bridge formations occur from outer shells to inner shells, resulting in a gradual salt-bridge formation and thus a continuous strength increase. The dynamic FT-IR spectra corresponding to the aging is shown in Fig. 7. The peaks at 1731, 1620, 1525 cm$^{-1}$ stand for free acid, salt, and free acid, respectively [34]. Apparently with aging, 1731 and 1525 became smaller and smaller but 1620 became larger and larger, indicating a gradual slat-bridge formation.

TABLE II. ND COMONOMER ON COMPRESSIVE PROPERTIES

|   | [I][1] | Co-M[2] | YS [MPa] | CS [MPa] | M [GPa] |
|---|---|---|---|---|---|
| A | 1 % | MBA | 91.3 (5.4) | 183.6 (16)[a] | 4.01 (0.6)[c] |
| B | 1 % | HEMA | 51.2 (1.8) | 148.9 (3.2)[b] | 1.60 (0.0)[e] |
| C | 2 % | MBA | 79.4 (3.1) | 187.9 (7.0)[a] | 3.68 (0.3)[c, d] |
| D | 2 % | HEMA | 38.7 (1.7) | 155.3 (1.1)[b] | 1.82 (0.1)[e] |
| E | 3 % | MBA | 62.1 (4.1) | 155.5 (6.8)[b] | 3.07 (0.1)[d] |
| F | 3 % | HEMA | 29.3 (0.9) | 127.3 (2.0) | 1.55 (0.1)[e] |

[1][I] = 3-arm BPB initiator concentration; [2]Co-M = comonomer; Entries are mean values with standard deviations in parentheses and the mean values with the same superscript letter were not significantly different (p > 0.05). Filler = Fuji II LC; Grafting ratio of IEM = 50% (by mole); Polymer/MBA/water = 50:25:25 (by weight); and P/L ratio = 2.7. Specimens were conditioned in distilled water at 37 °C for 24 h prior to testing.
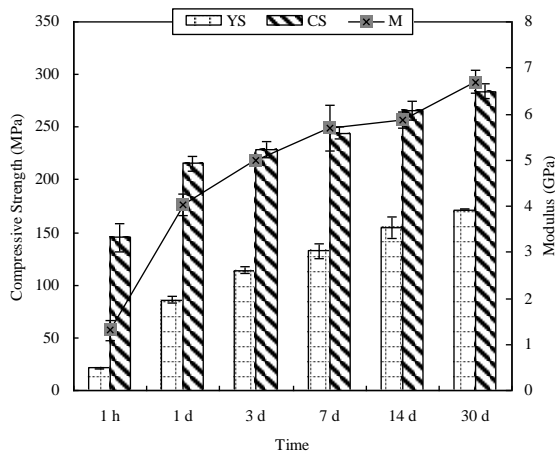
*Fig. 6. Effect of aging on compressive properties: MW of 3-arm PAA = 4,274 Daltons; Filler = Fuji II LC; Grafting ratio = 50%; P/L ratio = 3.0. Polymer/MBA/water = 50:25:25. Specimens were conditioned in distilled water at 37 $^{o}C$ for 24 h.*
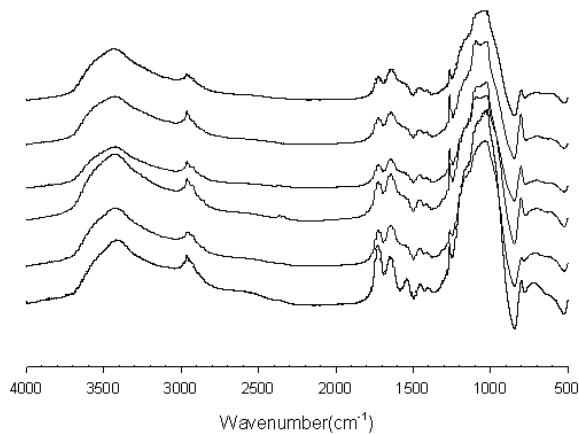


*Fig. 7. FT-IR spectra of the cured cements based on aging: The absorbance spectra corresponding to those cements studied in Fig. 6. The broken cements were ground right after testing, freeze-dried and mixed with KBr for FT-IR evaluation.*

## IV. CONCLUSIONS

A light-curable 3-arm star-shape polyacrylic acid was synthesized via aqueous ATRP. The reaction was run at room temperature in the presence of water. The reaction was extremely fast with huge exotherm generation and the 90 % conversion was achieved only at 10 min. The effects of MW and comonomer on strengths were significant. It was found that the MBA-containing cements exhibited much higher CS than the HEMA-containing cement due to salt-bridge contribution of the MBA. Increasing P/L ratio increased CS. In the course of aging, the novel cement showed a continuous increase in yield strength, ultimate strength and modulus in compression within 30 days, indicating that a salt-bridge formation is a gradual process. Future studies will focus on optimization of the system, evaluation of other properties such as bonding to tooth and fluoride release, and biocompatibility test.

REFERENCES

[1] D.C. Smith, "Development of glass-ionomer cement systems", Biomaterials, vol. 19, pp. 467-478, 1998.

[2] A.D. Wilson, J.W. McLean, Glass-ionomer cements, Chicago, IL: Quintessence Publ Co., 1988.

[3] C.L. Davidson, I.A. Mjör, Advances in glass-ionomer cements, Chicago, IL: Quintessence Publ Co., 1999.

[4] A.D. Wilson, "Resin-modified glass-ionomer cement", Int. J. Prosthodont., vol. 3, pp. 425-429, 1990.

[5] P. Hotz, J.W. McLean, I. Sced, A.D. Wilson, "The bonding of glass-ionomer cements to metal and tooth substrates", Br. Dent. J., vol. 142, pp. 41-47, 1977.

[6] W.R. Lacefield, M.C. Reindl, D.H. Retief, "Tensile bond strength of a glass-ionomer cement", J. Prosthet. Dent., vol. 53, pp. 194-198, 1985.

[7] L. Forsten, "Fluoride release from a glass-ionomer cement", Scand. J. Dent. Res., vol. 85, pp. 503-504, 1977.

[8] R.G. Craig, J.M. Power, Restorative Dental Materials, 11th ed., St Louis, MO: Mosby-Year Book, Inc., 2002.

[9] J.W. Nicholson, J.H. Braybrook, E.A. Wasson, "The biocompatibility of glass-poly(alkenoate) glass-ionomer cements: a review", J. Biomater. Sci. Polym. Edn., vol. 2(4), pp. 277-285, 1991.

[10] W.R. Hume, G.J. Mount, "In vitro studies on the potential for pulpal cytotoxicity of glass-ionomer cements", J. Dent. Res., vol. 67(6), pp. 915-918, 1988.

[11] R. Guggenberger, R. May, K.P. Stefan, „New trends in glass-ionomer chemistry", Biomaterials, vol. 19, pp. 479-483, 1998.

[12] S. B. Mitra, "Adhesion to dentin and physical properties of a light-cured glass-ionomer liner/base", J. Dent. Res., vol. 70, pp. 72-74, 1991.

[13] Y. Momoi, K. Hirosaki, A. Kohno, J.F. McCabe, "Flexural properties of resin-modified hybrid glass-ionomers in comparison with conventional acid-base glass-ionomers", Dent. Mater. J., vol. 14(2), pp. 109-119, 1995.

[14] D. Xie, B.M. Culbertson, W.M. Johnston, "Formulations of light-curable glass-ionomer cements containing N-vinylpyrrolidone", J. M. S. Pure Appl. Chem., vol. A35(10), pp. 1631-1650, 1998.

[15] D. Xie, W. Wu, A. Puckett, B. Farmer, J. Mays, "Novel resin modified glass ionomer cements

with improved flexural strength and ease of handling", Eur. Polym. J., vol. 40(2), pp. 343-351, 2004.

[16] E.C. Kao, B.M. Culbertson, D. Xie, "Preparation of glass-ionomer cement using N-acryloyl-substituted amino acid monomers: evaluation of physical properties", Dent. Mater., vol. 12, pp. 44-51, 1996.

[17] D. Xie, I-D. Chung, W. Wu, J. Lemons, A. Puckett, J. Mays, "An amino acid modified and non-HEMA containing glass-ionomer cement", Biomaterials, vol. 25(10), pp. 1825-1830, 2004.

[18] D. Xie, B.M. Culbertson, W.M. Johnston, "Improved flexural strength of N-vinylpyrrolidone modified acrylic acid copolymers for glass-ionomers", J. M. S. Pure Appl. Chem., vol. A35(10), pp. 1615-1629, 1998.

[19] P. Bahadur, N.V. Sastry, Principles of Polymer Science, Boca Raton, FL: CRC press, 2002.

[20] C.F. Huang, H.F. Lee, S.W. Kuo, H. Xu, F.C. Chang, "Star polymers via atom transfer radical polymerization from adamantine-based cores", Polymer, vol. 45, pp. 2261-2269, 2004.

[21] K. Matyjaszewski, J. Xia, "Atom transfer radical polymerization", Chem. Rev. vol. 101, pp. 2921-2990, 2001.

[22] W. Geurtsen, W. Spahl, G. Leyhausen, "Residual monomer/additive release and viability in cytotoxicity of light-curing glass-ionomer cements and compomers", J. Dent. Res., vol. 77 (12), pp. 2012-2019, 1998.

[23] C.A. de Souza Costa, J. Hebling, F. Garcia-Godoy, C.T. Hanks, "In vitro cytotoxicity of five glass-ionomer cements", Biomaterials, vol. 24, pp. 3853–3858, 2003.

[24] K.L. Robinson, M.A. Khan, M.V. de Paz Ba´n˜ez, X.S. Wang, S.P. Armes, "Controlled polymerization of 2-hydroxyethyl methacrylate by ATRP at ambient temperature", Macromolecules, vol. 34, pp. 3155-3158, 2001.

[25] X.S. Wang, S.P. Armes, "Facile ATRP of methoxy-capped oligo(ethylene oxide) methacrylate in aqueous media at ambient temeprature", Macromolecules, vol. 33, pp. 6640-6647, 2000.

[26] E.J. Ashford, N.C. Billingham, S.P. Armes, First example of the ATRP of an acidic monomer: direct synthesis of methacrylic acid copolymers in aqueous media", Chem. Commun., pp. 1285-1286, 1999.

[27] X.S. Wang, R.A. Jackson, S.P. Armes, "Facile synthesis of acidic comonomers via ATRP in aqueous media at ambient temeprature", Macromolecules, vol. 33, pp. 255-257, 2000.

[28] I.D. Chung, P. Britt, D. Xie, E. Harth, J. Mays, "Synthesis of amino acid-based polymers via atom transfer radical polymerization in aqueous media at ambient temperature", J. Chem. Commun., pp. 1046-1048, 2005.

[29] D. Xie, M. Faddah, J.G. Park, "Novel amino acid modified zinc polycarboxylates for improved dental cements", Dent. Mater., vol. 21, pp. 739-748, 2005.

[30] E.J. Ashford, V. Naldi, R. O'Dell, N.C. Billingham, S.P. Armes, "First example of the atom transfer radical polymerisation of an acidic monomer: direct synthesis of methacrylic acid copolymers in aqueous media", Chem. Commun., pp. 1285–1286, 1999.

[31] D. Xie, W.A. Brantley, B.M. Culbertson, G. Wang, "Mechanical properties and microstructures of glass-ionomer cements", Dent. Mater., vol. 16(2), pp. 129-138, 2000.

[32] D. Xie, B.M. Culbertson, G. Wang, "Microhardness of N-vinylpyrrolidone modified glass-ionomers cements", J. M. S. Pure Appl. Chem., vol. A35(4), pp. 547-561, 1998.

[33] D. Xie, I-D. Chung, W. Wu, J. Mays, "Synthesis and evaluation of HEMA-free glass-ionomer cements for dental applications", Dent. Mater., vol. 20, pp. 470-478, 2004.

[34] A.M. Young, "FTIR investigation of polymerisation and polyacid neutralization kinetics in resin-modi.ed glass-ionomer dental cements", Biomaterials, vol. 23, pp. 3289–3295, 2002.