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A novel light-cured glass-ionomer system for improved dental restoratives

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Abstract A novel light-cured glass-ionomer cement (LCGIC) system based on the 4-arm star-shape poly (acrylic acid) (AA) tethered with glycidyl methacrylate has been developed. The 4-arm poly(AA) polymer was synthesized using atom-transfer radical polymerization. The purified polymer was used to formulate with water and Fuji II LC filler to form LCGICs. Compressive strength (CS) was used as a screening tool for evaluation. The effects of grafting ratio, polymer/water (P/W) ratio, filler powder/polymer liquid (P/L) ratio and aging on strengths were investigated. All the specimens were conditioned in distilled water at 37 °C for 24 h prior to testing. The results show that the 4-arm poly(AA) polymer exhibited a lower viscosity as compared to its linear counterpart that was synthesized via conventional free-radical polymerization. This novel LCGIC system was 13% in CS, 86% in diametral tensile strength (DTS) and 123% in flexural strength higher but 93.6% in shrinkage lower than Fuji II LC. Increasing P/W ratio significantly increased both CS and DTS. Upon increasing grafting ratio, the CS was increased from 35% to 50% but not from 50% to 70%. Likewise, when P/L ratio was increased, the CS was increased from 2.2 to 2.7 but not from 2.7 to 3.0. During aging, the ultimate CS (MPa) was significantly increased from 209.2 at 1 h to 329.7 at 1 week. It appears that this novel LCGIC system will be a better dental restorative because it demonstrated improved mechanical strengths as well as little shrinkage and may eliminate cytotoxicity in current LCGICs caused by leached HEMA.

Introduction

It is known that glass-ionomer cements (GICs) are 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 25 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].

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 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) [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

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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 GIC formulations have been linear polymers and 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 (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.

Although light-cured RMGICs have demonstrated reduced moisture sensitivity, improved mechanical strengths, extended working time and ease of clinical handling [1, 4], there have been concerns regarding their biocompatibility [9, 10]. It has been found that RMGICs are less biocompatible than CGICs [22, 23]. The reason is attributed to 2-hydroxyethyl methacrylate (HEMA) and the other low molecular weight species such as additives and co-initiators in RMGIC formulations [22]. HEMA is incorporated as the major and necessary component in RMGIC formulations for enhancing water solubility of the methacrylate-containing polyacids because HEMA bears both hydroxyl and methacrylate groups. So far almost all the commercially available RMGICs contain HEMA [1, 4, 22]. Free HEMA leached from RMGICs such as Vitremer and Compoglass has been reported to exhibit cytotoxicity when it contacts the dental pulp tissue and osteoblasts [24, 25]. Theoretically speaking, almost all the low molecular weight molecules are cytotoxic to the cells or tissues more or less [26]. That is why CGICs show little cytotoxicity to dental pulp or the other tissues [22, 23]. However, as we know, by using current technologies it is almost impossible to formulate a RMGIC without incorporating any low MW amphiphilic molecules like HEMA. In this paper, we also hypothesized to tether amphiphilic methacrylate functionality onto the proposed star-shape polyalkenoic acid to substitute very hydrophobic methacrylate moieties currently being used in RMGICs [1, 4] and eliminate HEMA, which may provide a promising route for formulating a very biocompatible RMGIC for improved dental and orthopedic applications.

The objective of this study was to synthesize and characterize novel 4-arm star-shape poly(AA) via ATRP technique, tether in situ light-curable amphiphilic methacrylate functionality onto the polyacid backbone, use this light-curable star-shape poly(AA) to formulate a comonomer-free RMGIC, and evaluate the mechanical strengths of the formed cements.

Materials and methods

Materials

Pentaerythritol, triethylamine (TEA), 2-bromoisobutyryl bromide (BIBB), CuBr, *N,N,N′N′N′N″*-pentamethyldiethylenetriamine (PMDETA), dl-camphoroquinone (CQ), diphenyliodonium chloride (DC), 2,2′-azobisisobutyronitrile (AIBN), pyridine, tert-butyl acrylate (t-BA), glycidyl methacrylate (GM), anhydrous magnesium sulfate ($MgSO_4$), sodium hydroxide (NaOH), hydrochloric acid (HCl, 37%), diethyl ether, N'N-dimethylformamide (DMF), tetrahydrofuran (THF), methanol (MeOH), deuterated methyl sulfoxide, and ethyl acetate were used as received from VWR International Inc (Bristol, CT) without further purifications. AIBN was re-crystallized in methanol before use. GC Fuji II^{TM} LC glass powders were supplied by GC America Inc (Alsip, IL).

Synthesis and characterization

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 [27]. Briefly, to a reactor charged with 100 ml of TEA, 15 g of pentaerythritol and 200 ml of THF, a mixture of 100 ml of BIBB in 25 ml of THF was added dropwise with stirring at room temperature. After addition was completed, additional one hour 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).

Synthesis of the 4-arm poly(AA) via ATRP

To a flask containing dioxane (5.0 g), a mixture of 4-arm initiator (1% by mole), PMDEMA (3%, ligand) and t-BA (5.0 g) was charged. The CuBr (3%) was incorporated under N_2 purging after the above solution was degassed and nitrogen-purged via three freeze-thaw cycles. The solution was then heated to 120 °C to initiate the ATRP [28]. FT-IR was used to monitor the reaction. After the polymerization was completed, the poly(t-BA) polymer was precipitated from water. CuBr and PMDEMA were removed by re-precipitated from dioxane/water. The

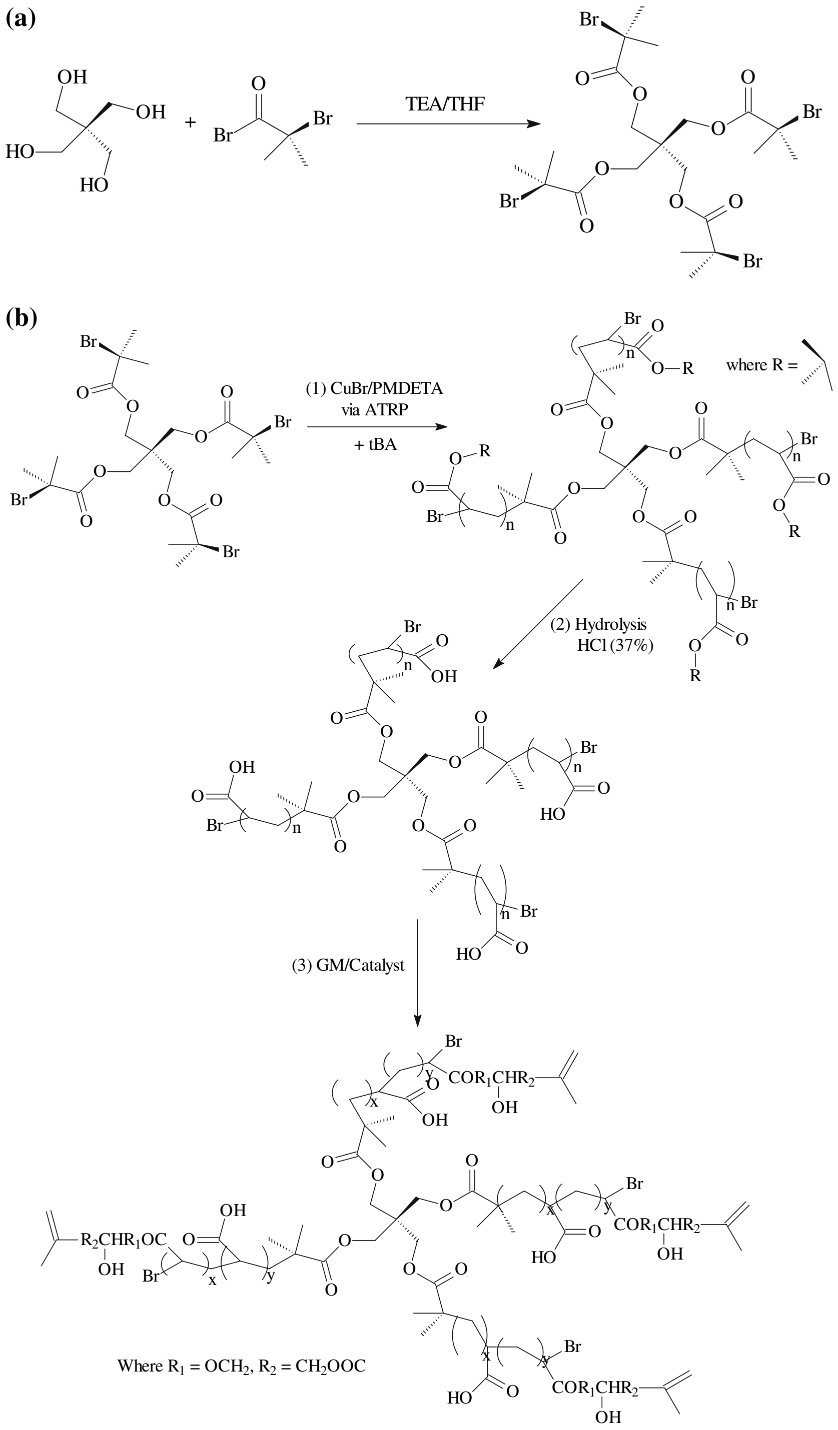

Fig. 1 Schematic diagram for synthesis: (**a**) Synthesis of the 4-arm initiator; (**b**) Synthesis of the 4-arm poly(t-BA) via ATRP, hydrolysis of the 4-arm poly(t-BA) and GM tethering

colorless poly(t-BA) polymer was then hydrolyzed in a mixed solvent of dioxane and HCl (37%) [29] (dioxane/HCl = 1/3) under refluxed condition for 18 h. The formed poly(AA) was dialyzed against water until the pH became neutral. The purified 4-arm poly(AA) was obtained after freeze-dried. The reaction scheme for the polymer synthesis via ATRP is described in Fig. 1(b).

Synthesis of the linear poly(AA) via conventional free-radical polymerization

Linear poly(AA) was synthesized following our previous publication [30]. Briefly, to a flask containing AIBN and THF, a mixture of AA and THF was added dropwise. Under a nitrogen blanket, the reaction was initiated and run at 62 °C for 10 h. The polymer was purified by precipitation using ether and drying in a vacuum oven.

Synthesis of the GM-tethered4-arm poly(AA)

Typically, to a three-neck flask containing the 4-arm poly(AA) (4.1 g), THF (18 ml) and BHT (1%, by weight), a mixture of GM (3.6 g), THF (21 ml), and pyridine (1% of GM, by weight) was added dropwise. Under a nitrogen blanket, the reaction was initiated and run at 60 °C for 5 h and then kept at room temperature overnight. FT-IR spectroscopy was used to monitor the reaction. The polymer tethered with GM was recovered by precipitation from diethyl ether, followed by drying in a vacuum oven at 23 °C. The yield was greater than 95%. The scheme for synthesis of the GM-tethered 4-arm poly(AA) is described in Fig. 1b.

Characterization of the 4-arm initiator and polymers

The synthesized 4-arm initiator was characterized by melting point identification, Fourier transform-infrared (FT-IR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy. The polymers were characterized by FT-IR, NMR and vapor pressure osmometry. The GM-tethered polymers were identified by FT-IR and NMR spectroscopy. The melting point was measured using a digital melting point apparatus (Electrothermal IA9000 Series, Electrothermal Engineering Ltd., Essex, United Kingdom). 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 as a solvent. MW was determined in DMF using a vapor pressure osmometer (K-7000, ICON Scientific, Inc., North Potomac, MD). The viscosities of the liquid formulated with the poly(AA) and distilled water (1:1, by weight) as well as the liquid formulated with the GM-tethered 4-arm poly(AA) and distilled water in different weight ratios were determined at 23 °C using a programmable cone/plate viscometer (RVDV-II + CP, Brookfield Eng. Lab. Inc., Middleboro, MA).

Evaluation

Formulation and preparation of specimens for strength tests

The cements were formulated with a two-component system (liquid and powder) [17]. The liquid was formulated with the GM-tethered polymer, water, 0.7% CQ (photo-initiator, by weight), 1.4% DC (activator) and 0.05% HQ (stabilizer). Fuji II LC glass powder was used to formulate the cements with a powder/liquid (P/L) ratio of 2.7. 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 by 8 mm length for compressive strength (CS) and 4 mm diameter by 2 mm length for diametral tensile strength (DTS) tests. A split Teflon mold with dimensions of 3 mm in width × 3 mm in thickness × 25 mm in length was used to make rectangular specimens for flexural strength (FS) test. A transparent plastic window was used on the top of the split mold for light exposure. Specimens were exposed to blue light (EXAKT 520 Blue Light Polymerization Unit, 9W/71, GmbH, Germany) for 1 min, followed by conditioned in 100% humidity for 15 min, removed from the mold and conditioned in distilled water at 37 °C for 24 h unless specified, prior to testing.

Strength measurements

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 for CS, DTS and FS measurements. The FS test was performed in three-point bending, with a span of 20 mm between supports. The sample sizes were $n = 6$–8 for each test.

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, and DTS was determined from the relationship $DTS = 2P/\pi dt$, where P = the load at fracture, d = the diameter of the cylinder and t = the thickness of the cylinder. FS was obtained using the expression $FS = 3Pl/2bd^2$, where P = the load at fracture, l = the distance between the two supports, b = the breadth of the specimen, and d = the depth of the specimen.

Determination of polymerization shrinkage

The polymerization shrinkage of the cement was determined using an equation of % Shrinkage = (1–$d_{uncured}$/d_{cured}) × 100, where d_{cured} = density of cured cement and $d_{uncured}$ = density of uncured cement [31]. The densities of the uncured and cured cements were determined by weighing the cement paste, injected from a calibrated syringe, and weighing the cured cylindrical specimens, whose volumes were measured in a calibrated buret in the presence of hexane, respectively. The mean values were averaged from three readings.

Statistical analysis

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 $\alpha = 0.05$ was used for statistical significance.

Results and discussion

Characterization

The purified 4-arm BIBB initiator was white crystal (melting point = 135–136 °C and yield = 45%). Figure 2(a) shows the FT-IR spectra for both BIBB and 4-arm BIBB. The characteristic peaks are listed below: (1) BIBB (cm^{-1}): carbonyl: 1808 and 1767 (C=O stretching, strong) and 944 (C=O bending); C–Br: 848, 626 and 599 (C–Br bending); CH_3: 1459, 1371 and 1112 (CH_3 bending) and 2975–2950 (weak C–H stretching). (2) 4-arm BIBB: carbonyl: 1738 (C=O stretching, strong) and 1271 (C–O–C stretching); C–Br: 1164 (C–Br bending); CH_3: 1390, 1372, 1106 and 984 (CH_3 bending) and 2976–2933 (C–H stretching). It is clear that the significant shift of carbonyl group from two peaks at 1808 and 1767 to one peak at 1738 and disappearances of 944 and 848 strongly confirmed the formation of the 4-arm BIBB, along with the clear measured melting point (135–136 °C) of the 4-arm BIBB.

Figure 2(b) shows the FT-IR spectra for t-BA, 4-arm poly(t-BA), 4-arm poly(AA) and GM-tethered 4-arm poly(AA). The t-BA shows multiple peaks in its spectrum. Among them, 1722 and 1636 are the two most characteristic peaks associated with carbonyl and carbon-carbon double bond, respectively. In contrast, disappearance of the peak at 1636 in the spectrum for the 4-arm poly(t-BA) confirmed the completion of polymerization. After hydrolysis of poly(t-BA), a broad and significant peak at 3600–2300 and a strong but wider peak at 1714.5 can be observed as compared to poly(t-BA). The former is the typical peak for hydroxyl group on carboxylic acid (OH stretching) whereas the latter is the characteristic peak for carbonyl stretching on poly(AA). In contrast, the GM-tethered poly(AA) shows five typical peaks: 3600–2400 cm^{-1} (OH stretching on COOH); 3434 (OH on tethered methacrylate); 1716.9 (C=O stretching on COO); 1636.1 (C=C bending); and 1508.4 (C=O of COO-C on tethered methacrylate). It is apparent that the peaks at 3434, 1636 and 1508 cm^{-1} on the GM-tethered 4-arm poly(AA) identified the difference between the 4-arm poly(AA) and GM-tethered 4-arm poly(AA).

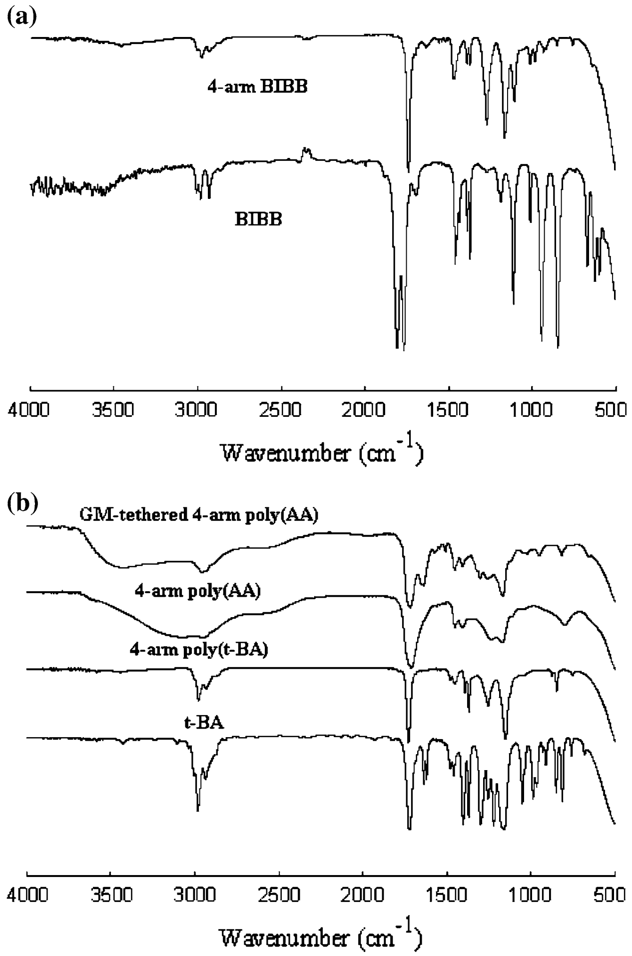

Fig. 2 FT-IR spectra for the initiator and polymers: (**a**) BIBB and 4-arm BIBB initiator; (**b**) 4-arm poly(t-BA) and 4-arm poly(AA)

Figure 3 shows the ^{1}HNMR spectra for 4-arm BIBB, 4-arm poly(AA) and GM-tethered 4-arm poly(AA). The chemical shifts of the 4-arm BIBB initiator were found as follows (ppm): a: 4.3 (CH_2) and b: 1.9 (CH_3). The chemical shifts of the 4-arm poly(AA) were listed below (ppm): a:

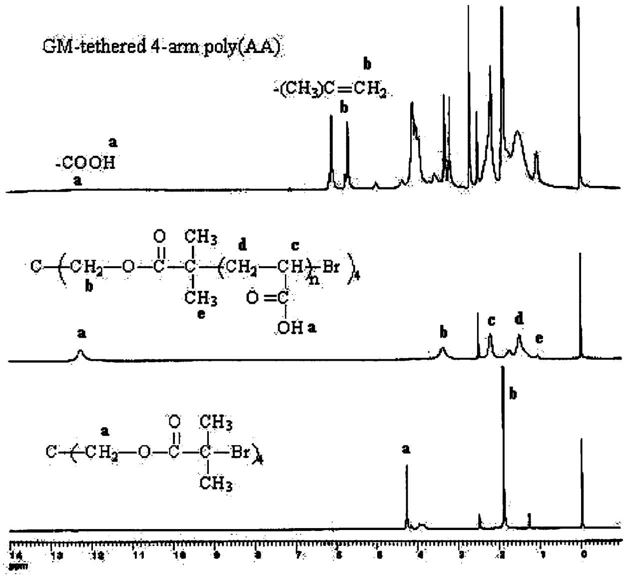

Fig. 3 ^{1}HNMR spectra for the initiator and polymers: Top: GM-tethered 4-arm poly(AA); Middle: 4-arm poly(AA); Bottom: 4-arm BIBB

12.25 (COOH); b: 3.4 (CH_2); c: 2.25 (CH); d: 1.8 and 1.55 (CH_2); and e: 1.1 (CH_3). The typical chemical shifts for the GM-tethered 4-arm poly(AA) were shown below (ppm): a: 12.30 (COOH) and b: 5.70 and 6.10 ($C{=}CH_2$). The chemical shift for COOH on the GM-tethered 4-arm poly(AA) was weak but broad. The characteristic chemical shifts at 12.25 and 5.70 as well as 6.10 identified the difference among the three materials.

The molecular weights (MWs) of the synthesized 4-arm poly(AA) via ATRP and linear poly(AA) via conventional free-radical polymerization were characterized using VPO and shown in Table 1. The conversions of the polymers were determined using FT-IR spectra and they all are greater than 97%. The viscosities were measured using a cone & plate viscometer and shown in Table 1. It is obvious that the 4-arm poly(AA) even with a MW of 18,066 showed a lower viscosity value than the linear poly(AA) (not measurable), although the latter's MW were only 9,704. This is probably attributed to the former' s spherical nature.

Table 1 Conversion, MW and viscosity of the synthesized polymers

Code	Polymer	Conversion[1]	M_n[2]	Viscosity (cp)[3]
A	4-arm poly(AA)	97.5	18,066	148.6
B	Linear poly(AA)[4]	99.9	9,704	N/A[5]

[1] Conversion of the polymer was measured from FT-IR spectra; [2]M_n (number average MW) of the poly(AA) was determined in DMF via a vapor pressure osmometer; [3]Viscosity of the polymer aqueous solution (poly(AA):distilled water = 1:1, by weight) was measured using a cone & plate viscometer at 23 °C; [4]Linear poly(AA), which was synthesized via conventional free-radical polymerization using 1% AIBN as initiator; [5] N/A means not measurable due to gel formations

Synthesis

Synthesis of the 4-arm poly (AA)

It is known that almost all the poly(alkenoic acid)s being used in current dental GICs are linear polymers and are synthesized via conventional free-radical polymerization. No reports have been found so far on study of different architectures of polyacids for GIC applications. One of the main reasons may be attributed to the fact that it is impossible to synthesize polymers with different architectures by using conventional free-radical polymerization techniques. Atom-transfer radical polymerization (ATRP), a recently developed technology for controlled radical polymerization, is capable of making various architectures such as star polymers and block copolymers [21]. By using such a technique, we were able to synthesize novel star-shaped (or spherical) poly(AA) in this study. Figure 4 shows a semi-logarithmic plot of the ATRP of t-BA in dioxane (a) and a kinetic plot of monomer to polymer conversion versus time (b). The polymerization was initiated by the 4-arm BIBB, catalyzed by CuBr-PMDETA complex and run at 120 °C. The plot of ln ($[M]_0/[M]$) versus time (Fig. 4a), where $[M]_0$ = the initial concentration of the monomer and [M] = the monomer concentration at any time, is almost linear, suggesting that the polymerization propagation was constant throughout the reaction or in other words, a constant concentration of growing radicals reflects a first-order kinetics. From the kinetic plot of monomer to polymer conversion versus time (Fig. 4b), it is apparent that the monomer conversion increased with time. The reaction in dioxane took 3 h to reach a 90% conversion and 5 h to reach a 97% conversion. In order to make sure that the t-BA was polymerized only by ATRP but not by heat-initiated conventional free-radical polymerization, a parallel experiment without any initiator involved was conducted under the same condition. It was found that no polymer was generated within 8 h, which indicates that the poly(t-BA) was polymerized by the ATRP reaction. The 4-arm poly(AA) was prepared by hydrolysis of the poly(t-BA) in a mixed solvent of dioxane and aqueous HCl (37%) for 8–12 h under refluxed condition [24], followed by dialysis against water until the pH reached neutral.

Synthesis of the GM-tethered 4-arm poly(AA)

The reaction between GM and carboxylic acid on poly (AA) took about fourteen hours to complete. Disappearance of the epoxy group on GM at 761 cm^{-1} (FT-IR)

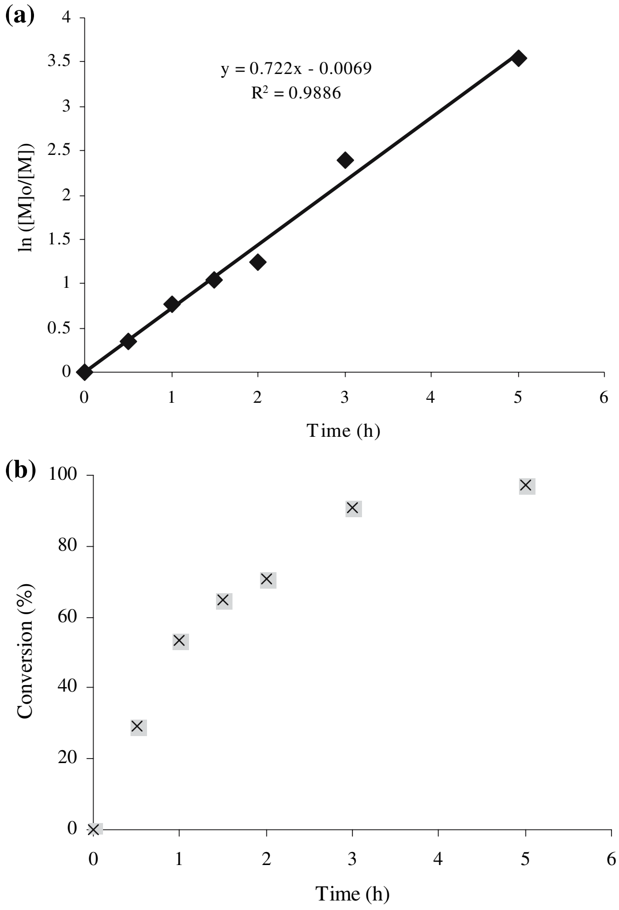

Fig. 4 Conversion and kinetic plot of the 4-arm poly(t-BA) derived from the FT-IR absorbance spectra: (**a**) Conversion vs. time curve; (**b**) First-order kinetic plot of ln ($[M]_o/[M]$) vs. time. The 4-arm poly (t-BA) was prepared in dioxane via ATRP in the presence of the 4-arm BIBB, CuBr and PMDETA

confirmed the completion of the tethering reaction. The completion of the tethering of GM was also confirmed by the fact that the yield was greater than 95%.

Evaluation

Significance of tethering of GM onto the 4-arm poly(AA)

As we know, the main difference between RMGICs and CGICs is their liquid composition [4]. The liquid in RMGICs is composed of HEMA, photo-initiators, water, and a poly(alkenoic acid) having pendent in situ polymerizable methacrylate on its backbone [12, 14] or a mixture of poly(alkenoic acid) and methacrylate-containing monomer/oligomer [13]. The liquid in CGICs consists of only hydrophilic poly(alkenoic acid) and water [1, 2]. Due to introduction of hydrophobic methacrylate functionality, amphiphilic monomers such as HEMA have to be incorporated into the RMGIC liquid formulation to enhance the solubility of the hydrophobic poly(alkenoic acid) in water. It is known that almost all the low MW molecules are cytotoxic to cells or tissues [26]. This is typically true to HEMA when it is used in dentistry [22, 24] or orthopedics [25]. Without these amphiphilic small molecules like HEMA, however, it seems impossible to formulate RMGICs by using current technologies [1, 4]. Our previous research has shown that tethering GM onto the poly(alkenoic acid) backbone can increase water-solubility of the polyacid because of introduction of hydroxyl groups [32] as compared to 2-isocyanatoethyl methacrylate (IEM)-tethered poly(alkenoic acid) [12, 14, 17]. If we take a close look at the chemical structure of the GM-tethered 4-arm poly(AA) as shown in Fig. 1(b), it is apparent that each GM molecule produces one extra hydroxyl group when epoxy group on GM reacts with carboxyl group on poly(AA). Unlike IEM-tethering, these hydroxyl groups should actually make the GM-tethered poly(AA) less hydrophobic or to say the least they should not change the original hydrophilicity of the poly(AA) much. To take an advantage of the hydrophilic nature of the GM-tethered poly(AA), we proposed to formulate a novel comonomer-free RMGIC for potentially improved biocompatibility. However, we also noticed that these hydroxyl groups might reduce the mechanical strength and increase the viscosity. That is because on one hand these hydroxyl groups can absorb water and serve as a hydrogel, which might lead to a strength reduction, but on the other hand they can make a contribution to hydrogen bond formation, which might result in an increased viscosity. To overcome these shortcomings, we proposed (1) to synthesize the star-shaped 4-arm poly(AA) for a reduced viscosity and (2) to increase the relative hydrophilic GM-tethered poly(AA) content in the liquid formulation for an enhanced hydrophobicity and thus for an improved mechanical strength. The first strategy was to take advantage of star-shaped polymer's low-viscosity nature to overcome high viscosity of a linear polyacid. The second strategy was to offset the hydrophilic nature of the GM-tethered polymer by increasing polymer content in the liquid formulation. Fortunately, the outcome to the first strategy worked, i.e., the star-shaped (or spherical) 4-arm poly(AA) did show a reduced viscosity even at a higher MW as compared to its linear counterpart (see Table 1). The outcome to the second strategy will be discussed in the following section, i.e., the effect of polymer/water (P/W) ratio on compressive properties.

Effects of polymer/water ratio and grafting ratio on compressive properties

To study the effects of P/W ratio (by weight) and grafting ratio (by mole) on strengths, we formulated seven liquid solutions (C to I) based on the 4-arm poly(AA) tethered

Table 2 Effects of polymer/water ratio and GM grafting ratio on compressive properties

Code	P/W ratio	Grafting ratio	YS [MPa][1]	Modulus [GPa]	UCS [MPa][2]	Viscosity (cp)[3]
C	50/50	35%	47.5 (8.2)[4]	2.65 (0.82)	68.5 (7.2)	75.6
D	60/40	35%	81.8 (6.0)	5.00 (0.25)^{b,c}	124.8 (9.4)^{e}	275.2
E	75/25	35%	143.2 (2.7)	6.43 (0.18)^{d}	166.8 (9.9)^{f}	3323
F	60/40	50%	91.9 (4.2)	4.85 (0.18)^{b}	146.5 (6.9)	171.5
G	75/25	50%	170.3 (1.9)	6.62 (0.06)^{d}	245.8 (4.1)^{g}	1764
H	60/40	70%	105.5 (7.9)^{a}	5.19 (0.25)^{c}	159.7 (7.6)^{f}	206.4
I	75/25	70%	164.0 (1.1)	6.89 (0.33)^{d}	256.0 (5.8)^{g}	2094
B*[5]	75/25	50%	105.4 (7.7)^{a}	5.43 (0.34)^{c}	126.5 (7.7)^{e}	6830

[1] YS = CS at yield; [2]UCS = ultimate CS; [3]Viscosity of GM-tethered polymer/water solution was determined at 23 °C; [4]Entries are mean values with standard deviations in parentheses and the mean values with the same superscript letter were not significantly different ($p > 0.05$). [5]B* = linear poly(AA), which was synthesized via conventional free-radical polymerization and tethered with GM. Specimens were conditioned in distilled water at 37 °C for 24 h

with GM and one liquid solution (B*) based on the linear poly(AA) tethered with GM. Three P/W ratios including 50/50, 60/40 and 75/25 and three grafting ratios including 35%, 50% and 70% were studied. Table 2 and Fig. 5 show the results of CS and DTS of the cements prepared from the above formulations. Table 2 also shows the viscosities of the corresponding polymer solutions. The cements C, D and E represent the 35% GM-tethered 4-arm poly(AA)s with the P/W ratio at 50/50, 60/40 and 75/25. It is obvious that increasing P/W ratio significantly increased yield compressive strength (YS), modulus and ultimate CS (UCS), which indicates that a higher polymer concentration can enhance the mechanical strengths of the relative hydrophilic GM-tethered poly(AA) cement. Meanwhile, the viscosity of the polymer solution was also increased due to increased polymer contents. The cement C showed the lowest YS (47.5 MPa), modulus (2.65 GPa) and UCS (68.5 MPa), which implies that at 50/50, the hydrophilic characteristic of the GM-tethered poly(AA) prevails and the cement behaves like a hydrogel. However, increasing polymer content in water overcomes the disadvantage exhibited by the hydroxyl groups from the GM-tethered poly(AA) and makes the cement stronger. Next, we studied the effect of grafting ratio on the strength by changing grafting ratio from 35% to 70%. It was found that at P/W = 60/40 increasing grafting ratio significantly increased YS and UCS but not necessarily modulus. However, at 75/25, increasing grafting ratio did significantly increase the CS values from 35% to 50% but did not change the CS much when the ratio reached 70%. In other words, there was no statistical difference between the 50% and 70% GM-tethered cements at 75/25, which may be attributed to inconsistent mixing because we did have some difficulty in mixing when grafting ratio = 70% and P/W ratio = 75/25. The highest strength values fell between 50% (170.3 MPa in YS, 6.62 GPa in modulus and 245.8 MPa) and 70% GM-tethered 4-arm poly(AA) cements (164.0 MPa, 6.89 GPa and 256.0 MPa) at P/W ratio = 75/25. Interestingly the ultimate CS values (245.8 and 256.0 MPa) were very close to the optimal CS (259.1 MPa) of the amino-acid derivative-modified RMGICs reported from our previous study [17]. This result is very encouraging because it has demonstrated the feasibility of eliminating low MW comonomers in RMGIC formulations, which may greatly improve the biocompatibility of current commercially available light-cured GICs. We also noticed that the viscosity values were increased when the P/W ratio increased. Furthermore, the polymer solutions with 35% GM showed a higher viscosity as compared to those with 50% and 70%

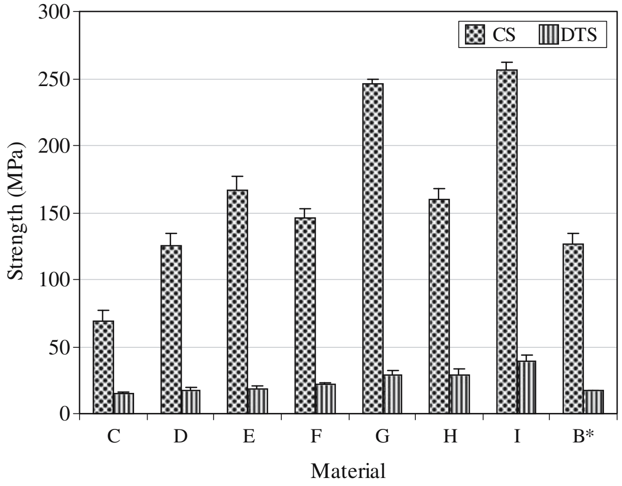

Fig. 5 CS and DTS of the light-cured GM-tethered poly(AA)-constructed cements: The codes, P/W ratio and grafting ratio are described in Table 2; Filler = Fuji II LC; P/L ratio = 2.7. Specimens were conditioned in distilled water at 37 C for 24 h prior to testing

GM, which can be attributed to a relatively strong hydrogen bond formation in the polymer solution with 35% GM because less GM tethering means more free acid on the polymer backbone. In contrast, the linear poly(AA) (B*) that was synthesized via conventional free-radical polymerization showed much lower strengths (YS = 105.4 MPa, modulus = 5.43 GPa and UCS = 124.5) but much higher viscosity (6830 cp) than those for corresponding 4-arm poly(AA) cement (G, 170.3, 6.62, 245.8 and 1764). As we know, it is hard to increase strengths of the linear poly(AA) only by increasing MW because increasing MW increases hydrogen bond formations resulting from the ordered linear poly(AA) structure [2, 16, 18]. However, the result indicates that the star-shape 4-arm poly(AA) can overcome the shortcoming generated by the ordered linear poly(AA). The data from DTS showed the similar trend to those from CS. The order of DTS (MPa) was: I (39.5 ± 4.6) > G (29.3 ± 2.4) > H (29.1 ± 4.5) > F (21.3 ± 2.0) > E (18.4 ± 2.2) > D (17.3 ± 2.2) > N (14.4 ± 2.0). Both CS (256.0 MPa) and DTS (39.5 MPa) of the 70% GM-tethered cement at a P/W ratio of 75/25 were the highest among all the GM-tethered 4-arm poly(AA)-constructed cements.

Effect of glass powder/polymer liquid ratio on compressive properties

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 [33, 34], 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 and 3.0) on CS and the results are shown in Table 3. A significant increase in YS, modulus and UCS was observed when the P/L ratio was increased from 2.2 to 2.7 but not from 2.7 to 3.0. No statistical difference in YS, modulus and UCS was found between 2.7 and 3.0, which can be attributed to inconsistent mixing because we did experience a difficult mixing at P/L ratio = 3.0.

Table 3 Effects of P/L ratio and aging on compressive properties

Parameter	YS [MPa][1]	UCS [MPa][2]	Modulus [GPa]
Effect of P/L ratio[4]			
2.2	144.2 (1.3)[3]	204.7 (1.8)	5.86 (0.30)
2.7	164.0 (1.1)[a]	256.0 (5.8)[b]	6.89 (0.33)[c]
3.0	170.4 (2.1)[a]	244.2 (2.1)[b]	6.94 (0.21)[c]
Effect of aging[5]			
1 h	78.1 (2.8)	209.2 (6.5)	2.59 (0.02)
1 d	164.0 (1.1)	256.0 (5.8)	6.89 (0.33)
1 w	252.9 (3.1)	329.7 (11)	8.12 (0.29)

[1] YS = CS at yield; [2]UCS = ultimate CS; [3]Entries are mean values with standard deviations in parentheses and the mean values with the same superscript letter were not significantly different ($p > 0.05$); [4]Grafting ratio = 70% and P/W ratio = 75/25; Specimens were conditioned in distilled water at 37 °C for 24 h; [5]Grafting ratio = 70%, P/W ratio = 75/25 and P/L ratio = 2.7. Specimens were conditioned in distilled water at 37 °C prior to testing

Aging

It is known that GICs increase their strengths with time due to constant salt-bridge formations [3]. The optimal 70% GM-tethered 4-arm poly(AA) cement was conditioned at 37 °C in distilled water for 1 h, 1 day and 1 week, followed by CS determinations. As shown in Table 3, the compressive strengths were significantly increased from 78.1 to 252.9 MPa in YS, 2.59 to 8.12 GPa in modulus, and 209.2 to 329.7 MPa in UCS within one week. This result was quite consistent with those reported from numerous studies [3, 35, 36].

Comparison between the experimental cement and commercial control

Finally, we measured the FS and polymerization shrinkage of the optimal experimental cement and compared the measured CS, DTS, FS and shrinkage with those of commercial Fuji II LC cement. The strengths of both cements were determined after conditioned in distilled water at 37 °C for 24 h and the polymerization shrinkage was measured immediately after being light-cured. As shown in Table 4, the light-cured experimental cement showed significantly

Table 4 CS, DTS, FS and shrinkage comparisons between the experimental cement and Fuji II LC

Material	CS [MPa]	DTS [MPa]	FS [MPa]	Shrinkage (%)
Experimental cement[1]	258.1 (5.8)[3]	39.5 (4.6)	98.4 (5.0)	0.3 (0.02)
Fuji II LC[2]	228.2 (6.4)	21.2 (1.1)	44.2 (3.4)	4.7 (0.13)

[1] Grafting ratio = 70%, P/W ratio = 75/25 and P/L ratio = 2.7; [2]P/L ratio = 3.2/1 (per manufacturer's recommendation); [3]Entries are mean values with standard deviations in parentheses. Specimens for CS, DTS and FS tests were conditioned in distilled water at 37 °C for 24 h prior to testing. Specimens for shrinkage measurement were tested immediately after being light-cured

higher CS (256.0 ± 5.8 MPa), DTS (39.5 ± 4.6 MPa) and FS (98.4 ± 5.0 MPa) but much lower shrinkage (0.3 ± 0.02%) as compared to corresponding 228.2 ± 6.4, 21.2 ± 1.1, 44.2 ± 3.4 and 4.7 ± 0.13 for Fuji II LC. Higher mechanical strengths and low or little shrinkage can be attributed to the nature of this unique comonomer-free and pendent hydroxyl group-containing system as compared to Fuji II LC, because Fuji II LC cement contains HEMA and other low MW methacrylate comonomers [13].

Conclusions

This study developed a novel light-cured GIC system based on the 4-arm star-shape poly(AA) tethered with glycidyl methacrylate. The 4-arm poly(AA) polymer was synthesized using ATRP. The synthesized polymer showed a lower viscosity as compared to its linear counterpart that was synthesized via conventional free-radical polymerization, which is probably attributed to the spherical nature of the former. The GM-tethered 4-arm poly(AA)-constructed LCGICs showed significantly high mechanical strengths even without any comonomers involved. The effect of polymer/water (P/W) ratio was significant, i.e., increasing P/W ratio significantly increased both CS and DTS. However, with increasing grating ratio, CS was only increased from 35% to 50% and no statistical change was observed between 50% and 70%. For the effect of P/L ratio, CS was increased only from 2.2 to 2.7 and no statistical change was found between 2.7 and 3.0. In the course of aging, YS, modulus and UCS were significantly increased from 78.1, 2.59 and 209.2 at 1 h to 252.9 MPa, 8.12 GPa and 329.7 MPa at 1 week, respectively. The selected optimal experimental cement was 13% in CS, 86% in DTS and 123% in FS higher as well as 93.6% in shrinkage lower than Fuji II LC. It appears that this novel comonomer-free LCGIC system will be a better dental restorative because it demonstrated improved mechanical strengths as well as little shrinkage and may eliminate cytotoxicity in current LCGICs caused by leached HEMA. Future studies will focus on optimization of the system, evaluation of other properties such as bonding to tooth and fluoride release, and biocompatibility test.

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