

Synthesis of iodine-containing cyclophosphazenes for using as radiopacifiers in dental composite resin



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ABSTRACT

In this study, a strategy of using iodine-containing cyclophosphazenes as radiopacifiers for dental composite resin was evaluated. It was hypothesized that cyclophosphazenes bearing both iodine and acrylate group were able to endow composite resins radiopacity without compromising mechanical properties. The cyclophosphazene compounds were synthesized by subsequently nucleophilic substitution of hexachlorocyclotriphosphazene with hydroxyethyl methacrylate (HEMA) and 4-iodoaniline. Cyclotriphosphazenes containing two different molar ratios of HEMA to 4-iodoaniline (1:5 and 2:4) were obtained, and were identified with ¹H NMR, FT-IR, UV and mass spectroscopy. The iodine-containing cyclophosphazenes were able to dissolve well in bisphenol A glycidyl methacrylate (Bis-GMA)/triethylene glycol dimethacrylate (TEGDMA) resin, and were added at two contents (10 or 15%wt. of the resin). The resins were photo-cured and post-thermal treated before characterizations. The resulting composite resins demonstrated the ability of blocking X-ray. And the addition of HEMA-co-iodoaniline substituted cyclotriphosphazenes caused minor adverse effect on the mechanical properties of the resins because the cyclotriphosphazenes could mix well and react with the resins. The presence of rigid phosphazene rings between resin backbones displayed an effective function of decreasing polymerization shrinkage. In summary, soluble and reactive iodine-containing cyclotriphosphazenes demonstrated advantages over traditional heavy metals or metal oxides in being used as additives for producing radiopaque dental resins.

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1. Introduction

Composite resins have been widely applied in dental clinic therapy as restorations, luting agents, base and core foundations, etc. [1]. To achieve efficient treatment, there is a growing interest to improve the properties of dental composite resins through years. The common challenges include improving mechanical properties, decreasing water sorption, reducing polymerization shrinkage, and increasing monomer conversion [2,3]. In addition, dental materials should be sufficiently radiopaque to be detected against a background of enamel and dentin for clinical diagnostic purposes. This property is quite useful not only to evaluate restoration, but also to monitor its long-term stability [2,4].

Acrylate-based resins such as bisphenol A glycidyl methacrylate (Bis-GMA) are the mostly used dental reparation materials, but they are radiolucent. Many approaches have been reported in attempting to give them some degree of radiopacity. Usually, radiopacifying agents such as heavy metal powders, inorganic salts of a heavy element, or organic compounds containing a heavy atom substituent were

physically blended with the polymer [5,6]. However, these attempts often suffered from mechanical and biocompatible problems that the resulted resins were clinically unacceptable [7,8]. Reactive metal salts of vinyl monomers such as barium and zinc acrylates, which were able to copolymerize with acrylate-based resins, could impart radiopacity to dental resins with a more homogeneous structure [9–11]. The ionic nature of these resins, however, led to a gradual loss of the opacifying atom due to water uptake and subsequent hydrolysis [12]. Halogen atoms such as iodine and bromine are quite radiopaque because of their high electronic densities. Therefore, vinyl monomers containing covalently bound iodine or bromine were chosen to copolymerize with other acrylic monomers to impart radiopacity [13,14]. They have been identified as good sources for radiopaque polymer matrixes [15–17]. The major issues of these iodine- or bromine-containing monomers are their reactivity and halogen content. The reported iodine- or bromine-containing monomers usually comprised an aromatic ring, halogen atoms and acrylate residues [18,19]. To achieve high stable radiopacity and fast reactions, cross-linkable monomers containing more than one acrylate group and one halogen atom are desired.

Cyclophosphazenes have a ring-structure with alternative phosphorus and nitrogen single and double bonds. There are two groups attaching to each phosphorus atom, which are

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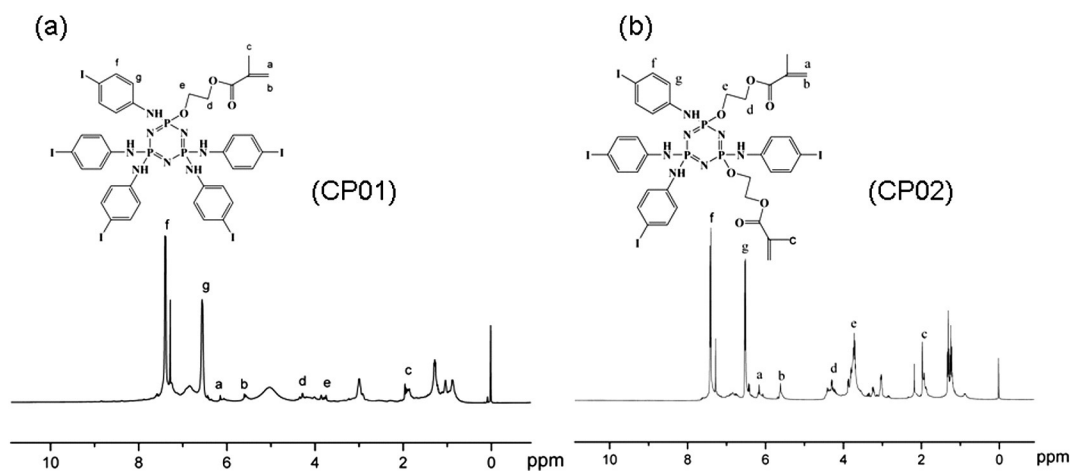


Fig. 1. ^1H NMR spectra of two HEMA-co-iodoaniline substituted cyclotriphosphazenes: (a) CP01 with HEMA to 4-iodoaniline ratio of 1:5; (b) CP02 with HEMA to 4-iodoaniline ratio of 2:4.

connected via nucleophilic substitution starting from chlorocyclophosphazenes such as hexachlorocyclotriphosphazene (HCCP, $\text{P}_3\text{N}_3\text{Cl}_6$) or octachlorocyclotetraphosphazene (OCCP, $\text{P}_4\text{N}_4\text{Cl}_8$) [20,21]. Six or eight functional groups are able to be attached, which provide the potential to bear several acrylate groups and halogen atoms at the same time. Thus, it is hypothesized that incorporating iodine-containing cyclophosphazene monomers into composite resins is a promising way to achieve sufficient radiopacity at low addition amounts. And their organic feature and crosslinkability are envisioned advantageous over traditional radiopacifiers in modifying the performance of composite resins. To this end, hydroxyethyl methacrylate (HEMA) and 4-iodoaniline co-substituted cyclotriphosphazenes were designed and synthesized via nucleophilic substitution of HCCP. The resulting cyclotriphosphazenes were then incorporated into Bis-GMA resins and copolymerized. Characterizations including mechanical properties, conversion of vinyl group, polymerization shrinkage and radiopacity were carried out to evaluate the possibility using HEMA-co-iodoaniline substituted cyclotriphosphazenes as radiopacifiers for dental composite resins.

2. Materials and methods

2.1. Materials

HCCP (Boyuan New Material Ltd., Ningbo, China) was recrystallized by using anhydrous hexane and subsequently sublimed under vacuum

(55 °C, ~0.1 mm Hg). HEMA (Alfa Aesar) and triethylamine (Beijing Chemical Works, China) were dehydrated by distilling from CaH_2 . Tetrahydrofuran (THF, Beijing Chemical Works, China) was dehydrated with sodium and distilled. Light-curable dental restoratives including Bis-GMA and triethylene glycol dimethacrylate (TEGDMA), as well as camphorquinone (CQ), 2-(dimethylamino) ethyl methacrylate (DMAEMA), and 4-iodoaniline were supplied by Sigma-Aldrich and used directly. All other reagents and solvents were of analytical grade and supplied by Beijing Chemical Reagent Co., Ltd. (Beijing, China).

2.2. Synthesis of HEMA-co-iodoaniline substituted cyclotriphosphazenes

The preparation of HEMA-co-iodoaniline substituted cyclotriphosphazenes was performed via subsequent nucleophilic substitution with HEMA and 4-iodoaniline. Briefly, the HCCP was dissolved in anhydrous THF with triethylamine (2:1 in molar ratio to P-Cl bond) being added. HEMA (1:6 or 2:6 in molar ratio to P-Cl bond) solution in THF was then added dropwise, and then the mixture was stirred continuously for 48 h at room temperature. Subsequently, iodoaniline/THF solution (5:6 or 4:6 in molar ratio to P-Cl bond) was added dropwise into the system. The reaction was continued for another 96 h at room temperature. The whole procedure was protected under dry nitrogen atmosphere to prevent oxidation. After the insoluble hydrochloride salts were removed by filtration, the resulting solution was concentrated by vacuum evaporation of THF. The remains were dissolved

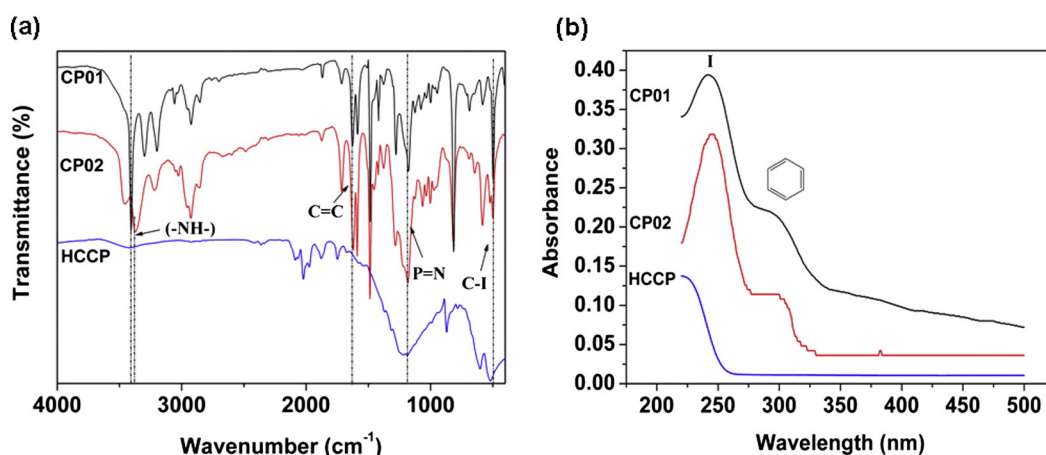


Fig. 2. FT-IR (a) and UV (b) spectra of HEMA-co-iodoaniline substituted cyclotriphosphazenes and HCCP control.

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