UV-Cleavable Polyrotaxane Cross-Linker for Modulating Mechanical Strength of Photocurable Resin Plastics

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Ⓢ Supporting Information

ABSTRACT: A UV-cleavable supramolecular cross-linker was designed to effectively control the mechanical strength of photocurable resin plastics. The resin monomer-soluble polyrotaxane (PRX) cross-linker was synthesized by introducing a hydrophobic *n*-butyl group and a cross-linkable methacrylate group in α-cyclodextrin threading to a polyethylene glycol containing UV-cleavable end groups. The UV-cleavable PRX cross-linker was completely dissolved in 2-hydroxyethytl methacrylate (HEMA) and camphorquinone, representative photocurable resin components. The dumbbell-like stiff resin plastic was prepared by irradiating the mixture with 450 nm blue light. The stiffened resin plastic maintained its ultimate tensile strength (UTS) under visible light irradiation. However, the UTS of the resin plastic was remarkably decreased to 40% of the original value once the plastic was exposed to 254 nm UV light. This indicates that the suggested UV-cleavable PRX cross-linker is effective in modulating the mechanical strength of photocurable resin plastics.
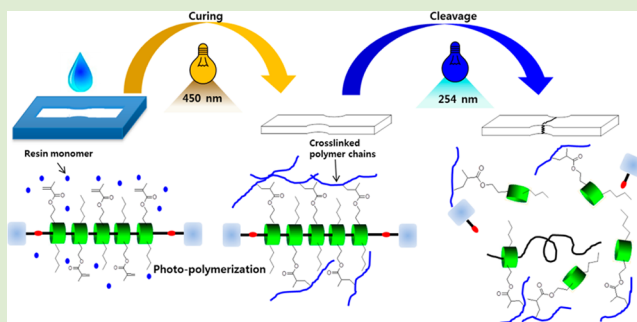
Photocurable resins are widely used in industry, commodities, and the biomedical field because they possess good formability, mechanical strength, and cost-effectiveness.[1,2] However, the irreversible stiffening of photocurable resins often causes significant problems in material applications in many engineering fields. For instance, photocurable resin plastic is essential to support prosthetic devices in the field of dentistry.[3] However, the irreversible stiffening of composite resins often causes significant damage to the dental tissue during removal after treatment.[4] Therefore, the development of stimuli-degradable resin plastic is highly desirable in dentistry.

The use of photolabile groups, such as *o*-nitrobenzyl, has many advantages in the design of degradable materials.[5−7] Unlike other degradable chemical groups, photolabile groups can be accurately triggered to cause degradation in both dry and wet conditions without additives.[8,9] The most general designs for photocleavable polymers use some form of photocleavable cross-linker. Both end groups of *o*-nitrobenzyl-containing chemicals can be modified with (meth)acrylate groups, and the modified chemical can be used as a photocleavable cross-linker to reversibly reinforce the mechanical strength of (meth)acrylic resins.[10] Structural materials requiring temporary mechanical strength, such as hydrogels, scaffolds, and photoetching materials, are generally designed using this concept.[11−16] Although the strategy is useful for the design of functional photocleavable materials, the efficiency of cleavage remains a critical problem. Because each photolabile group is designed to connect two (meth)acrylate groups,

equivalent amounts of photolabile groups with cross-linkable sites must be used to prepare the materials. For this reason, several minutes of irradiation with ultraviolet (UV) light is required to induce drastic degradation; the required time becomes much longer when the material is a rigid solid, such as a cross-linked resin.[17]

Polyrotaxane (PRX) is a supramolecule composed of a ring-shape host molecule, for example, α-cyclodextrin (α-CD), threaded on a linear guest molecule, for example, poly(ethylene glycol) (PEG).[18] This necklace-like molecular assembly is formed by noncovalent bonding; thus, the supramolecular assembly is rapidly collapsed when the end-capping groups of the guest molecule are removed.[19−21] Because several tens of α-CDs could be threaded on a single PEG chain, theoretically, several tens of cross-linkable sites or binding molecules on the α-CDs could be released at one time by a single end-group cleavage when PRX is used as a cross-linker with photolabile end-capping groups (Scheme 1). Therefore, a UV-cleavable PRX cross-linker is anticipated to be useful in effectively controlling the mechanical strength of cross-linked resins.

In the present study, we report the development of a UV-cleavable PRX cross-linker (photo-PRX) for the effective control of the mechanical strength of a photocurable resin plastic, which can be potentially applied to dental prosthetic

Scheme 1. Overall Concept of Preparing Resin Plastics Containing a UV-Cleavable PRX Cross-Linker
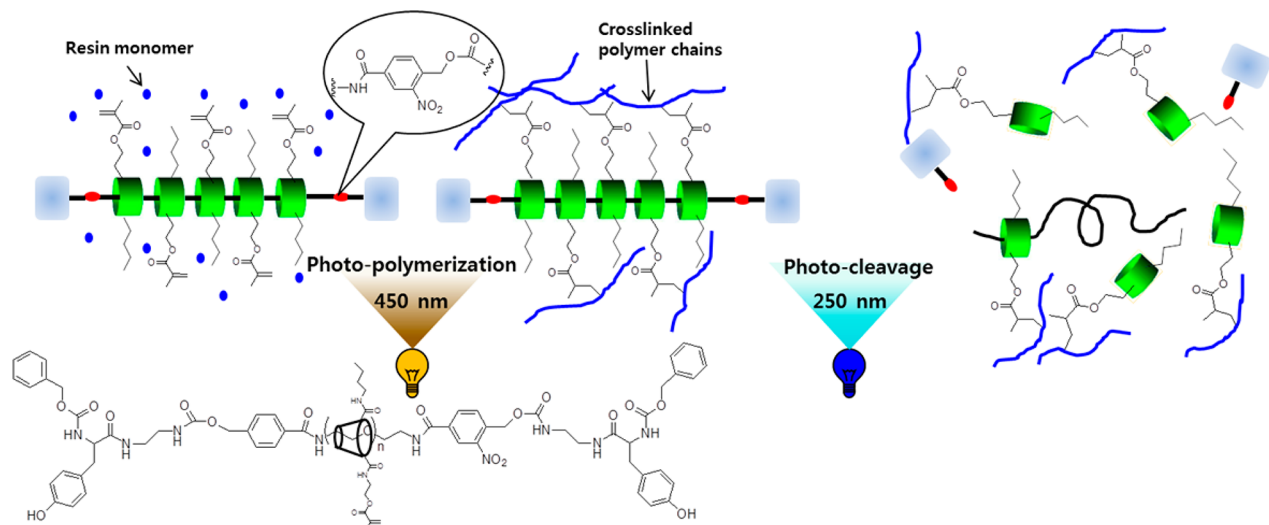
Table 1. Molecular Profile of Noncleavable and UV-Cleavable PRX Cross-Linker

symbol	composition			solubility	
	α-CD/PEG	n-butyl/α-CD	methacrylate/α-CD	in HEMA	with camphorquinone
cPRX	45	7.5	1.3	soluble	miscible
photo-PRX	30	8.0	1.0	soluble	miscible

materials. To this end, *o*-nitrobenzyl difunctionalized PEG bis(amine) (M_n: 10k) was synthesized as described in Scheme S1. Generally, the irradiation wavelength to photoset resins in dental prosthetic materials is within ~400−450 nm.[22] Because *o*-nitrobenzyl is usually cleaved by UV wavelengths of ~250−300 nm,[23] the photocuring and cleavage process were expected to be safely conducted. Using *o*-nitrobenzyl difunctionalized PEG, UV-cleavable PRX with 30 threaded α-CDs was successfully synthesized, as shown in Figure S4.

The most critical problem in the use of PRX derivatives is the poor solubility of PRX in organic solvents.[24] Because the photo-PRX must be directly mixed with a resin monomer, solubility in resin monomer species is a prerequisite to the design. Thus, we have prescreened the optimized PRX derivative that is directly soluble in various resin monomers used in dentistry.[25] When six or more hydroxyl groups on the threading α-CDs were substituted with *n*-butyl groups, the PRX was homogeneously dissolved in dental resin monomers such as 2-hydroxyethyl methacrylate (HEMA), methyl methacrylate (MMA), and triethylene glycol dimethacrylate (TEGDMA). In the present study, approximately eight *n*-butyl groups were introduced to each α-CD molecule, and one methacrylate group was further substituted for a residual hydroxyl group to provide cross-linking functionality. As a control, PRX cross-linker without a UV-cleavable end-group (cPRX) was also synthesized. Table 1 shows the overall molecular profile of the synthesized PRX cross-linkers. As shown, UV-cleavable and noncleavable PRX cross-linkers with similar compositions were successfully synthesized.

To investigate the maximum absorption wavelength of the synthesized PRX cross-linkers, UV−vis spectroscopy was conducted as shown in Figure 1a. The cPRX shows no significant absorption peak within the wavelength range of ~200−700 nm. Meanwhile, a strong absorption peak at ~240−270 nm is observed in the spectrum of the polymer solution
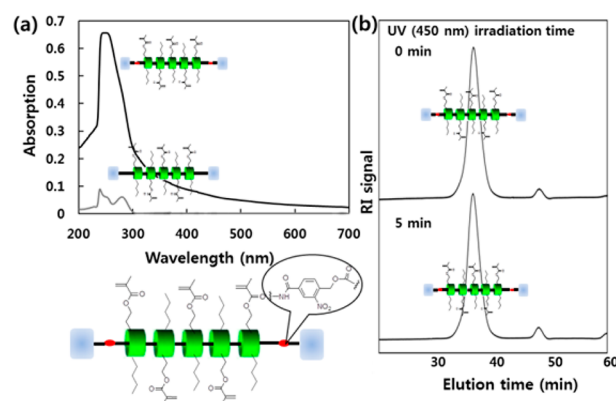

Figure 1. (a) UV−vis spectra for photo-PRX and control PRX cross-linker and (b) GPC chart of photo-PRX before and after irradiation by 450 nm light for 5 min.

containing photo-PRX. This is consistent with several previous studies on *o*-nitrobenzyl-containing organic molecules.[26] Although the photo-PRX shows this significant absorption peak at ~250 nm, no significant absorption peak is observed at ~450 nm, the wavelength required for camphorquinone-induced photopolymerization.[27] To confirm that irradiation-induced cleavage does not occur during the photocuring process, the PRX solution was exposed to the cross-linking wavelength of 450 nm for 5 min and gel permeation chromatography (GPC) was conducted. As a result, the photo-PRX cross-linker shows no significant degradation even after 5 min of irradiation by a 450 nm light (Figure 1b). This indicates that photo-PRX cross-linker could be safely used in the preparation of resin plastics.

The UV-cleaving of the photo-PRX within the ~240−270 nm wavelength range was also confirmed by GPC before and after UV irradiation (254 nm, 2.02 mW/cm^2) of the PRX

solutions. Figure 2 shows the resulting GPC charts taken before and after UV irradiation. Before irradiation, the GPC charts of
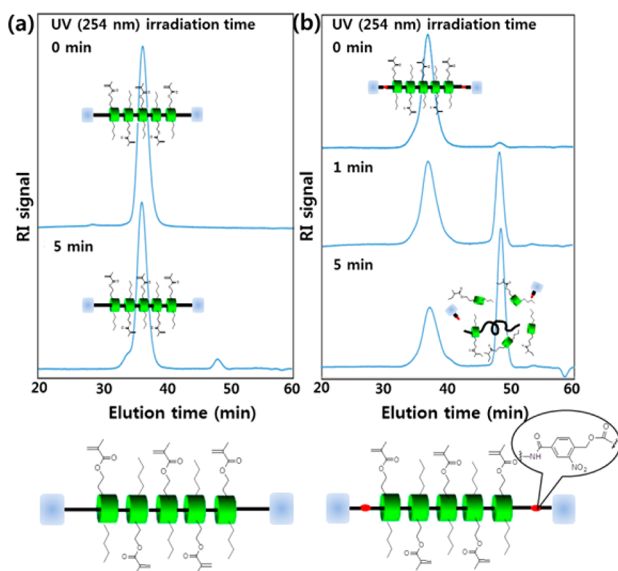

Figure 2. GPC charts of (a) cPRX and (b) photo-PRX taken before and after irradiation to 254 nm UV for each given time, respectively.

both PRX cross-linkers show unimodal macromolecular peaks near 36 min of retention time with a negligible peak intensity in the low-molecular-weight region (over 45 min). In the case of the cPRX cross-linker, no significant change in peak distribution is observed after 5 min UV irradiation. On the contrary, a rapid increase of the peak in the low-molecular-weight region (~48 min) is observed for the photo-PRX after 1 min UV irradiation. Because the retention time of the generated low-molecular-weight peak coincides with that of α-CD molecules, this peak-generation is attributed to the release of α-CD molecules after the cleavage of the o-nitrobenzyl end-capping unit.

The peak integration ratio of the released α-CD molecules is further increased from 45.4% to 65.2% when the irradiation time is increased from 1 to 5 min. Contrary to the rapid increase in peak integration ratio within the initial 1 min irradiation, the increase rate was almost saturated to ~70% when the irradiation time was further increased after 5 min. Because the synthesis of the o-nitrobenzyl end-functionalized PEG proceeded in multiple steps, ~30% of nonfunctionalized PEG was assumed to be included in the final product. This nonfunctionalized PEG may result in some noncleavable PRX cross-linker, which is thought to cause the residual PRX peak, even after a long exposure to UV light. In any event, the possibility of developing stimuli-weakened resin plastic, which is demanded in the field of dentistry for temporal splint and cementation, was successfully confirmed.

To confirm whether the UV-cleavable nature could be applied for modulating the mechanical strength of cross-linked resin plastics, 9 wt % of each PRX cross-linker was dissolved in HEMA with 4 wt % camphorquinone to prepare dumbbell-like resin plastic samples.

The transparent mixtures were transferred to dumbbell-like molds and irradiated by 450 nm blue light (530 mW/cm^2) for 2 min. Figure 3 shows a picture of the prepared samples. As shown, homogeneously transparent resin plastics are successfully formed by simple irradiation.
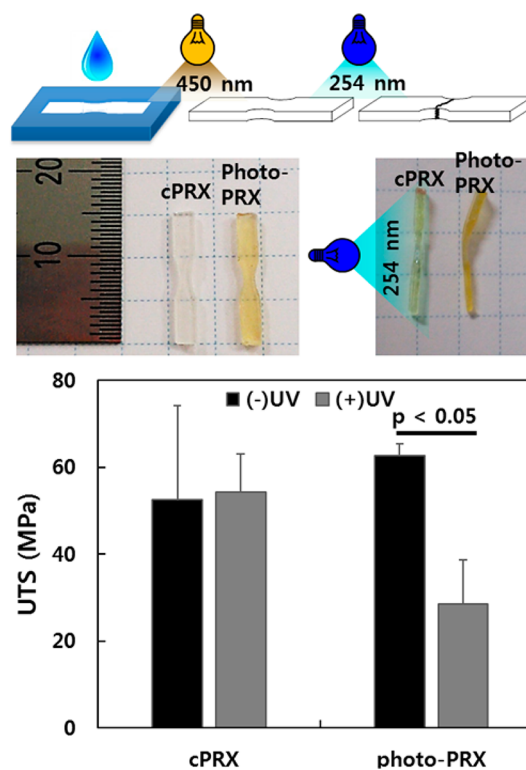

Figure 3. Schematic of preparing plastic specimens, photograph images of dumbbell-like resin plastics and side views of the specimens after irradiation of one side by 254 nm UV, UTS changes before and after UV irradiation of specimens (1 min for top side and 1 min for bottom side).

The characteristic light yellow color of the photo-PRX-containing sample may be induced by the o-nitrobenzyl groups.[28] The ultimate tensile strength (UTS) of the prepared resin plastics were then tested before and after irradiation by 254 nm UV (1 min for top side and another 1 min for bottom side of the resin plastic samples). As shown, the resin plastic containing cPRX as a cross-linker shows no significant change in UTS value after UV irradiation. This indicates that the cross-linking density of the resin plastic is not significantly changed by UV irradiation, reflecting the general behavior of irreversibly stiffened photocured dental resins.[29] In contrast, the UTS value of the resin plastic containing photo-PRX as a cross-linker is decreased to 40% of the initial value after UV irradiation. This indicates that the cross-linking network of the resin plastic was significantly degraded after only a 2 min UV irradiation. Generally, the UTS values of commercially available dental composite resins are ~50−90 MPa.[30] The prepared resin plastic shows UTS values of ~63 and 25 MPa before and after the irradiation, respectively; we conclude that our data reasonably presents the practicality of UV-cleavable dental resins by the addition of a supramolecular cross-linker.

In order to observe directly the disruption of the cross-linked network, thinner resin plastics containing 5 wt % PRX cross-linker were prepared; only one side of the specimens was irradiated to UV light (1 min). The specimen containing photo-PRX shows rapid bending within a 10 s irradiation time (Figure 3), while the cPRX specimen shows no shape change. This indicates that the polymer network of the irradiated side cross-linked by the photo-PRX is rapidly loosened by the drastic degradation of the cross-linker. Although the UTS of the sample prepared in this condition was not measurable because

of the bent structures, Figure 3 presents qualitative evidence that the UV-cleavable PRX cross-linker effectively modulates the mechanical strength of cross-linked dental resins.

Photocurable resin plastic is essential in many engineering fields, for example, in the field of dentistry to preserve the positions of prosthetic devices. However, the irreversible hardening of the resin plastic often causes significant damage to dental tissue when the prosthetic devices are removed after treatment. In the present study, we suggest a resin monomer-soluble and UV-cleavable supramolecular cross-linker that degrades with minimal end-group reactions. We expect that the presented concept could be applied to photocleavable resin plastics that could be utilized in many engineering fields, including dentistry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00619.

Experimental details and synthetic steps are explained with ^{1}H NMR charts (PDF).

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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