Abstract

Hollow polymer particles are widely used in various industries as coatings and thermal insulation materials. The encapsulation capabilities of various functional molecules and/or nanomaterials also provide access to applications such as drug delivery, heat storage, and catalysis, as well as self-healing materials. In this study, we successfully fabricated hollow polymer particles from poly(vinyl cinnamate) (PVC) particles using LED light (λ = 265 nm) through interfacial photocrosslinking. Furthermore, we systematically studied the effect of various parameters (solid contents of parent particles, photoirradiation time, photoirradiation power, and polymer chain length) on the polymer shell thickness of the hollow PVC particles fabricated by interfacial photocrosslinking. These findings are expected to further promote the use of hollow polymer particles in pharmaceutical and material applications.

KEYWORDS
interfacial photocrosslinking, poly(vinyl cinnamate)

1 INTRODUCTION

Polymer particles that possess internal void structures and hollow polymer particles are essential particulate materials that are widely used in various industries as coatings and thermal insulation owing to their unique physical properties. The encapsulation capabilities of various functional molecules and/or nanomaterials enable further applications, such as drug delivery, heat storage, catalysis, and self-healing materials. Therefore, many researchers have developed various fabrication routes to hollow/capsule polymer particles. The sacrificial template-assisted approach has been widely developed, in which sacrificial template particles (e.g., gold, silica, and calcium carbonate particles) are removed from a hierarchical polymer shell/inorganic template core structure, leading to the formation of hollow polymer particles. The construction of a polymer shell layer on a sacrificial template has been reported using layer-by-layer seeded polymerization, polyphenol-metal chelating, and surface-initiated polymerization approaches. The self-assembly of a phase-separated polymer (SaPSeP) is a unique and important approach for fabricating hollow and capsule-like particles. This approach is based on the polymerization-induced phase separation (or precipitation) of the prepared polymers, and the subsequent self-assembly of polymers at droplet/water interfaces. Interfacial polymerization in heterogeneous polymerization systems is another important approach for preparing hollow and capsule particles. Moreover, polymersomes (vesicles) formed by self-assembly or polymerization-induced self-assembly are used as hollow or capsule particles, and the physical properties of the polymersomes are improved by post-polymerization reactions.

Recently, our group developed interfacial photocrosslinking of the parent polymer particles as an approach for preparing hollow and capsule polymers. The photoinduced crosslinking reaction between different polymer chains only proceeds selectively in the particle interfacial region in this approach, where photocrosslinking is based on the [2π + 2π] photochemical alkene dimerization reaction. Removing the non-crosslinked polymers from the particle core region by washing after interfacial photocrosslinking leads to the formation of hollow polymer particles. Cinnamoyl, coumarin, and thymine groups have reportedly been used as photoactive groups. To date, polymethacrylates and polystyrene-based synthetic polymers that possess...
photoreactive groups have been used as parent polymer particles in interfacial photocrosslinking reactions, in which various parameters, such as photoirradiation power and time, polymer chain length, and parent particle concentration, potentially affect hollow particle fabrication. However, the effects of these parameters have not been systematically studied.

Herein, we systematically investigated the interfacial photocrosslinking process by examining the effects of photoirradiation time and power on the shell thickness of the hollow polymer particles fabricated by interfacial photocrosslinking using an LED light source ($\lambda = 265$ nm) capable of regulating light power. The effect of polymer chain length was also investigated by preparing various photoreactive polymers with different polymer chain lengths. Furthermore, we applied the interfacial photocrosslinking reaction to poly(vinyl alcohol) (PVA) derivatives [poly(vinyl cinnamate), (PVC)] for the first time, to fabricate hollow polymer particles in this study (Scheme 1). PVA is a biodegradable synthetic polymer$^{[36,37]}$ used industrially as adhesives,$^{[38,39]}$ films,$^{[40]}$ and heterogeneous polymerization stabilizers.$^{[41,42]}$ PVC was prepared as the photoreactive polymer by the esterification of PVA with cinnamoyl chloride. The insight into the interfacial photocrosslinking process obtained in this study is useful for creating and designing future hollow polymer particles.

2 | RESULTS AND DISCUSSION

2.1 | Preparing hollow PVC particles by interfacial photocrosslinking

Procedures for the synthesis of PVC have been reported by several groups.$^{[43,44]}$ In this study, PVC was prepared by the Schotten–Baumann reaction of PVA (degree of polymerization: 500, degree of saponification: $\sim$100%, PVA500) and cinnamoyl chloride in a biphasic system.$^{[43]}$ In this process, PVA was dissolved in a basic aqueous solution, which was then stirred with methyl ethyl ketone to dissolve the cinnamoyl chloride. After reaction completion, the obtained polymer was precipitated from methyl ethyl ketone using methanol (a poor solvent for PVC). After repeated precipitation to completely remove free cinnamoyl chloride (or cinnamic acid), the molecular structure of the obtained polymer was analyzed by $^1$H-NMR spectroscopy. New proton peaks that correspond to the cinnamoyl groups were observed in the $^1$H-NMR spectra (Figure 1). The integrated alkene/hydroxyl-proton peak ratio revealed that approximately 79% of the hydroxyl groups were cinnamoylated. Hence, PVC500 was successfully prepared by the Schotten–Baumann reaction of PVA500. The number-averaged molecular weight ($M_n$) and $M_w/M_n$ of PVC500 were determined to be approximately 37,000 and 2.2, respectively, by gel permeation chromatography (GPC). Here, $M_w$ is the weight-averaged molecular weight. The UV–vis spectrum of PVC500 exhibited a maximum absorbance at approximately $\lambda = 275$ nm that corresponds to the cinnamoyl groups (Figure 1). Furthermore, we evaluated the photoreactivity of a PVC500 thin film formed on a quartz substrate. The absorbance at 275 nm was lower after photoirradiation, consistent with $[2\pi + 2\pi]$ photocrosslinking reactions between cinnamoyl groups in the PVC500 film (Figure 1).

PVC500 particles for use as parent particles for interfacial photocrosslinking were then prepared by solvent evaporation. In the solvent evaporation method, the polymer is first dissolved in a volatile organic solvent, and the polymer solution is then homogenized in an aqueous medium.$^{[45,46]}$ Hence, the organic solvent must not be soluble in water. Chloroform was selected as a suitable organic solvent for the solvent evaporation method because PVC500 is highly soluble in it, is immiscible with water, and is highly volatile. The selection of a stabilizer is also important for particle
formation while maintaining high colloidal stability. We selected partially saponified PVA (polymerization degree: 1,000; saponification degree: 88%) as a stabilizer for the solvent evaporation process. Spherical polymer particles were successfully obtained by the solvent evaporation of PVC500 in chloroform and PVA (Figure 2). The PVC-500 particles were approximately 12.8 μm in size [number-averaged; coefficient of validation (CV): 33%].
Spherical PVC500 particles obtained after chloroform evaporation were photoirradiated with LED light ($\lambda = 265$ nm, 10 min, 0.3 mW/cm²) to form shell-crosslinked hollow polymer particles using an interfacial photocrosslinking reaction at a 6 mg/mL solid PVC particle content. The particle morphology does not appear to change during photoirradiation. The polymer particles retained their spherical shapes and sizes (approximately 13.7 $\mu$m, CV: 30%), as observed by optical microscopy (Figure 2). To remove the non-crosslinked polymers from the photoirradiated PVC500 particles, they were subjected to centrifugal washing with tetrahydrofuran (THF). A hollow internal structure was evidently observed in the PVC500 particles post centrifugal washing, which indicates that the photocrosslinking reaction proceeded in the PVC500 particles (Figure 2). Moreover, the washed PVC500 particles (~4.5 $\mu$m, CV: 32%) are not significantly different in size from the parent PVC500 particles, which indicates that the outermost shell regions of the PVC500 particles are crosslinked. In contrast, the non-photoirradiated polymer particles completely dissolved in THF. Furthermore, scanning electron microscopy (SEM) verified that the washed PVC500 particles have smooth surfaces and internal void structures, which strongly suggests that hollow PVC500 particles had been fabricated (Figure 2G). The polymer-particle photocrosslinking ratio was determined to be approximately 36% by UV–vis spectroscopy. For this, the absorbance of the removed (non-crosslinked) PVC500 was compared to that of the completely dissolved PVC500 particles (Figure 2). These results suggest that hollow polymer particles can be successfully fabricated onto PVC500 particles through interfacial photocrosslinking. Furthermore, small polymer particles are retained in the internal voids of the hollow particles, as shown in Figure 2. The remaining polymers are removed through the crosslinked shell layer with a suitable solvent to form a hollow structure following the interfacial photocrosslinking process. The polymers remaining in the hollow particles did not pass through the crosslinked shell layer; consequently, we believe that they are derived from high molecular weight PVC500 or photocrosslinked PVC500 that failed to form the hollow-particle crosslinked polymer shell layer. The small particles remaining in the washed polymer particles were determined to take up less than 1% (average: 0.53%, CV: 59%) of the total particle volume (Figure S1); consequently, the washed polymer particles are almost completely hollow.

The particle core region is photo-shielded by the non-crosslinked photoreactive groups during the interfacial photocrosslinking process. Hence, the solid content of the parent PVC particles may be an important parameter because the photo-shielding effect of the free cinnamoyl groups increases with increasing solid content. Actually, the interfacial photocrosslinking reaction proceeded slowly at high solid PVC particle contents; that is, the PVC shells of the particles became thinner with smaller (shrank) particle size as the solid PVC500 particle content increased from 6 to 30 mg/mL (Figure S2). Hence, we fixed the solid PVC particle content to 6 mg/mL in subsequent experiments.

2.2 Effect of photoirradiation time

The photocrosslinking reaction proceeds from the outermost layer of the polymer particles in the interfacial photocrosslinking approach because the outermost layer is directly photo-exposed. Meanwhile, the internal particle region is photoorradiated through the polymer layer, where unreacted free cinnamoyl groups within the polymer shell layer absorb light. Consequently, the unreacted free cinnamoyl groups shield the internal region from photoirradiation. The free cinnamoyl group density at the particle shell
layer gradually decreases as the photocrosslinking reaction proceeds from the outermost shell layer of the PVC particles, which may result in photocrosslinking reactions to the internal regions of the particles. Therefore, we investigated the effect of photoirradiation time on the formation of hollow particles at constant photoirradiation power. The PVC500 particles were photoirradiated for different times (5, 10, 15, and 20 min), after which they were washed with THF. Optical microscopy revealed that irrespective of photoirradiation time, these washed polymer particles are hollow with tiny particles included (Figure 3A–D). The PVC500 crosslinking ratio, which was determined from the absorbance of the removed PVC500, gradually increases with increasing photoirradiation time (Figure 3E,F). Furthermore, the hollow polymer shell thickness measured by optical microscopy gradually increases with increasing photoirradiation time (Figure 3H). Moreover, the average hollow polymer particle size was found to be independent of photoirradiation time (Figure 3G and Figure S3). The results also indicate that photoirradiation power can be used to control shell thickness.

2.3 Effect of photoirradiation power

Photoirradiation power is another important parameter that affects the interfacial photocrosslinking of photoreactive polymer particles because stronger light can access deeper regions within the polymer, resulting in the formation of thicker photocrosslinked polymer shells in the hollow polymer particles. To verify this hypothesis, we investigated the effect of photoirradiation power on shell thickness within the hollow polymer particles using PVC500 particles photoirradiated with light of various strengths (0.3, 0.9, 1.6, and 2.2 mW/cm²). Hollow polymer particles were successfully obtained when exposed to light with the abovementioned powers (Figure 4A–D). The hollow polymer particles prepared using different photoirradiation powers were similarly sized (Figure 4E and Figure S4). However, the polymer shell thickness was observed to gradually increase with increasing photoirradiation power (Figure 4F). These results indicate that photoirradiation power can be used to control shell thickness.

2.4 Effect of polymer chain length

Polymer chain length is an important parameter that affects polymer crosslinking reactions because the probability of branching between different polymer chains during the crosslinking reaction increases with increasing polymer chain length. We investigated the effect of polymer chain length on the thickness of the hollow polymer particle shell fabricated by interfacial photocrosslinking. Furthermore, we postulate why some of the polymers remain in the hollow polymer particles. That is, if the remaining polymer is derived from the as-prepared PVC, then the amount of polymer remaining inside the hollow particles will decrease with decreasing average PVA molecular weight. To confirm this, PVCs with different polymer chain lengths were prepared by the same procedure used to prepare PVC500 using PVA with different polymerization degrees (200, 300, and 1000). New 1H peaks derived from cinnamoyl groups
are observed in the $^1$H-NMR spectra of all synthesized PVCs (Figure S5). Cinnamoyl group introduction rates into PVC were determined to be approximately 78%, 74%, and 83% for PVC200, PVC300, and PVC1000, respectively. Furthermore, the newly prepared PVCs exhibit UV–vis spectra with absorption peaks at $\lambda_{\text{max}} = 275$ nm due to the cinnamoyl groups (Figure S6). In addition, the $M_n$ values of the PVC200, PVC300, and PVC1000 were determined to be approximately 17,900 ($M_w/M_n = 2.0$), 26,400 ($M_w/M_n = 2.1$), and 54,100 ($M_w/M_n = 2.8$), respectively, where molecular weights were calculated using polystyrene standards. These results confirm that PVCs with different polymer chain lengths were prepared.

PVC200, PVC300, and PVC1000 particles were prepared using the solvent evaporation method. The average PVC particle size was observed to gradually increase with increasing PVC polymer chain length when PVC droplets were prepared at the same homogenizer shearing speed, which is attributable to the increase in polymer solution viscosity during the homogenizer-promoted emulsification process, as polymer solution viscosity is related to the polymer molecular weight (Figure S7). The shearing speed was optimized for each PVC to obtain particles of similar size for PVCs with different chain lengths. Hollow PVC polymer particles were then prepared by interfacial photocrosslinking after optimizing the homogenization conditions for each PVC (Figure S7) Hollow PVC particles were successfully prepared in PVCs with different polymer chain lengths, as shown in Figure 5. SEM also revealed that hollow polymer particles were fabricated from all parent PVC particles. The PVC300, PVC500, and PVC1000 hollow particles have smooth surfaces, whereas the surfaces of the PVC200 hollow particles are wrinkled, which is possibly ascribable to the freeze-drying process (Figure 6). These results indicate that PVC200 is less mechanically strong than PVC300, PVC500, and PVC1000. The mechanical strengths of the hollow polymer particles prepared by the various interfacial photocrosslinking conditions will be investigated in the future. The shell thickness of the hollow PVC particles, evaluated by optical microscopy, gradually increased with increasing PVC polymer chain length (Figure 5). These results indicate that the PVC polymer chain length also affects the shell thickness of the hollow polymer particles prepared by interfacial photocrosslinking. During the photocrosslinking process, LED light with the same photoirradiation power was applied to all PVC particles for the same duration, with cinnamoyl groups of similar density. Therefore, the photocrosslinking reaction between the two cinnamoyl groups proceeded similarly in the particle-shell regions. The thinner shells of the hollow particles prepared using a lower PVC chain length indicate that a lower polymer chain length leads to higher amounts of photocrosslinked PVCs that do not form polymer shell layers in the hollow particles. Several tiny polymer particles are observed, including in the PVC200 hollow particles (Figure 6). These results reveal that the chain length of the photoreactive polymer affects the shell thickness of the hollow polymer particles by regulating the anchoring probability of the photocrosslinked polymers on the polymer shell layer.

3 CONCLUSIONS

In this study, we successfully created hollow PVC particles by interfacial photocrosslinking. PVC was prepared by the Schotten–Baumann reaction of PVA and cinnamoyl
chloride in a biphasic system, and spherical PVC particles were obtained following solvent evaporation. Photoirradiation and subsequent washing to remove non-crosslinked polymers from the PVC particles led to shell-crosslinked hollow polymer particles. Herein, we investigated in detail how photoirradiation time and power, as well as the PVC polymer chain length, affect the shell thickness of the obtained hollow particles; higher shell thicknesses were observed when the values of these parameters were increased. In particular, the thickness of the hollow particle shell can be controlled by changing the photoirradiation time and power in the interfacial photocrosslinking process. Furthermore, structural analysis of the prepared hollow polymers provides a detailed narrative of the various factors that affect the shapes and sizes of the prepared polymer particles, which is expected to promote the use of hollow polymer particles in pharmaceutical and material applications.

4 | EXPERIMENTAL SECTION

4.1 | Materials

Methyl ethyl ketone and NaOH were purchased from Nacalai Tesque (Kyoto, Japan). DMA, DIA, cinnamoyl chloride, and acryloxethyl thio carbamoyl rhodamine B were purchased from Sigma Aldrich (St. Louis, MO, USA). Chloroform, THF, and PVA (degree of polymerization: 1000, degree of saponification: 88% and 100%) were purchased from Wako Pure Chemical Co., Ltd. (Osaka, Japan). PVA (degree of polymerization: 200, 300, and 500, degree of saponification: 100%) was kindly supplied by JAPAN VAM & POVAL Co., Ltd (Osaka, Japan). Deionized (DI) water was obtained using a Millipore Milli-Q purification system.

4.2 | Apparatus

UV–vis spectroscopy was conducted using a V-560 spectrophotometer (Jasco Ltd., Tokyo, Japan). $^1$H NMR spectra were recorded using a 400-MHz FT-NMR spectrometer (JNM-ECX400, FT-NMR system, JEOL Ltd., Tokyo, Japan). Optical microscopy images were obtained using an LSM5 exciter (Carl Zeiss, Germany). A homogenizer (POLYTRON PT 1600 E, Kinematica Inc., Bohemia, NY, USA) was used to emulsify the PVA aqueous solution. $M_g$ and $M_w$ were determined by gel permeation chromatography at 40°C (JASCO CO-2060) using two poly(styrene-co-divinylbenzene) gel columns (Tosoh Corp., TSK gel GMHHR-M and GMHHR-G3000, 7.8 mm i.d. × 300 mm) with THF as the eluent at a flow rate of 1.0 mL/min (JASCO PU-2089) and a refractive index (RI) detector (JASCO RI-2031). The columns were calibrated using polystyrene standards.

4.3 | Synthesis of PVC

This typical procedure was followed: PVA (0.6 g, OH: 14 mmol) was dissolved in water (15 mL). An aqueous NaOH solution (2 g/mL, 10 mL) was mixed with an aqueous PVA solution in a round-bottom flask. Methyl ethyl ketone (20 mL) dissolved in cinnamoyl chloride (3.5 g, 21 mmol) was added to the PVA aqueous solution, and the solution was mixed by stirring in an ice bath for 1 h, after which the reaction was allowed to proceed overnight at room temperature. The methyl ethyl ketone phase containing PVC was collected and the polymer was precipitated in methanol. The PVC obtained was further purified by reprecipitation using fresh methyl ethyl ketone and methanol. After purification, the obtained polymer was dried under vacuum. Side-chain
hydroxyl to cinnamoyl ester conversion was evaluated by 1H-NMR spectroscopy.

4.4 | Preparing polymer particles

The solvent evaporation method was used to prepare the photoreactive PVC particles. PVC (50 mg) was dissolved in chloroform (1 mL) and the solution was homogenized in an aequous PVC solution (25 mL, 0.0067 wt%) using a homogenizer at 12,000 rpm, 14,000 rpm, or 15,000 rpm for 1 min. The organic solvent in the polymer droplets slowly evaporated at room temperature with gentle stirring. The average sizes of more than 200 particles in the optical micrographs were determined using ImageJ software.[47]

4.5 | Interfacial photocrosslinking for hollow particle fabrication

This typical procedure for interfacial photocrosslinking was followed: PVC particles (solid content: 2 mg/mL) dispersed in 6-mL vials. The particle dispersion was photoirradiated followed: PVC particles (solid content: 2 mg/mL) dispersed in 6-mL vials. The particle dispersion was photoirradiated with gentle stirring at room temperature. Each PVC particle dispersion was then washed five times with THF by centrifugation.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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