Solution viscosity adjustable phloroglucinolcarboxylic acid / formaldehyde applied in extremely thin shell fusion target fabrication

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Abstract. Capsuliform fusion target was prepared by using the O/W/O emulsion process. Phloroglucinolcarboxylic acid / formaldehyde (PF) is expected to be used as the water phase (W) solution which then gelates to be the shell of the capsule. The density of the shell should be low to obtain high laser gain. Phloroglucinolcarboxylic acid had addition and condensation reaction with formaldehyde under basic condition to form linear polymer first. The nano-scale linear polymers were then linked via noncovalent interactions, such as hydrogen bonding, van der Waals, to continue the gelation process. The type and amount of the base catalyst used in the reaction can affect the polymerization of PF, including the gelation rate and gelation concentration. By changing the basic condition of the reaction, the proper viscosity of $9 \times 10^{-5}$ for capsuliform target fabrication was reached and extremely thin gel shell thickness of 17µm with low polymer concentration of 26.3mg/cm$^3$ was obtained.

1. Introduction
The fast ignition concept is one of the most attractive paths to inertial fusion energy while fuel cryogenic target [1-2] technology is a key issue in fast ignition realization experiment (FIREX). The target is usually capsuliform, ~500µm in diameter [3]. The shell first should have foam structures to support the fuel which consists of liquid or solid deuterium and tritium. Secondly, in order to get a high target gain in ignition experiment, the thickness of the form shell should be the thinner the better. By using the O/W/O emulsion process to fabricate capuliform target, high viscosity of the shell material introduces thin shell thickness [4]. Phenolic compounds are one kind of traditional shell materials. They are low in atomic number which is required in fusion target. However, the most common used resorcinol/formaldehyde is difficult to control its viscosity increase when it reaches a high value because resorcinol is trifunctional and formaldehyde is bifunctional. The additional and condensation reactions of these two finally form crosslinked polymer which leads to quick solution-to-gel change at high viscosity.

Phloroglucinolcarboxylic acid/ formaldehyde (PF), which has four substituent groups on the benzene ring, forms linear polymer but no crosslink when polymerizing with formaldehyde in the presence of a base catalyst [5]. Therefore, the viscosity of PF precursory solution undergoes a slow increase even at a high value [4]. The type and amount of the base catalyst used in the reaction can affect the polymerization of PF, including the viscosity change and gelation concentration. Therefore, by changing the basic condition of the reaction, the proper viscosity for capsuliform target fabrication was reached and extremely thin gel shell of low polymer concentration was obtained.
2. **Experiment section**

### 2.1. Materials
Phloroglucinolcarboxylic acid (1.25 g, Tokyo Chemical Industry, co., LTD) was uniformly dispersed into 12 mL of pure water by ultrasonication, and then 4-10 mmol of NaOH (Sigma Aldrich Japan) and 1.71 mL 37% formaldehyde (Nacalai Tesque, Inc.) were added and stirred at 70°C. Sixty five minutes later, the solution was cooled down in an ice bath for half hour as the precursor of the gel. Then, the PF solution was sealed in a vial to wait for gelation at room temperature. The viscosity of the solution was checked during the gelation process and the gelation time was recorded.

### 2.2. Measurements
Fourier transform infrared (FTIR) absorption spectra were measured on carefully dried samples embedded in KBr pellets.

UV transmission spectra were measured on the precursor of PF gel obtained under different amount of base catalyst using Hitachi U-3100 spectrophotometer.

3. **Result and discussion**

#### 3.1. Polymerization of phloroglucinolcarboxylic acid and formaldehyde
Phloroglucinolcarboxylic acid has four substituent groups on the benzene ring and has only two hydrogen positions left on the benzene ring to react with formaldehyde. In the presence of base catalyst, the phloroglucinolcarboxylic acid has addition and condensation reaction with formaldehyde to form methylene bridge (-CH₂-) which leads to the linear PF polymer. The sol-gel polycondensation is influenced by typical sol-gel parameters such as the temperature, pH and concentration of reactions. The polymerization leads to the formation of linear polymer [6-13].

Phloroglucinolcarboxylic acid first had addition reactions under basic conditions with formaldehyde to form nucleus on which the methylol groups then condense with each other to promote the growth of the nuclei. When the nucleated structure grows to nano-scale linear polymers, they are linked via noncovalent interactions such as hydrogen bonding, van der Waals and electrostatic interactions to promote gelation process.

#### 3.2. The viscosity control and the gelation rate
In order to get thin shell when using O₃/W/O₂ emulsion process to fabricate capuliform target, high viscosity of PF solution is necessary. The amount of the NaOH added was proved to have influence on the viscosity change and gelation rate. In the mixture which contained 2.94 mmol phloroglucinolcarboxylic acid and 8.35 mmol formaldehyde, 4.0 mmol, 3.2 mmol, 2.4 mmol and 1.6 mmol of NaOH were respectively added. The viscosities of these precursory solutions of PF gel obtained under different amount of base catalysed were checked and the changing tendencies with the time were shown in figure 1. The higher the catalyst amount, the more rapidly the viscosity increased and the shorter time was needed for gelation. The gelation times for these cases were respectively 4 hours in 4 mmol solution, 44 hours in 3.2 mmol solution and 144 hours in 2.4 mmol solution. As for 1.6 mmol NaOH case, the solution has no gelation phenomenon in 30 days.
3.3. Minimum shell thickness and gelation concentration

According to the above data, the PF solution obtained under 3.2 mmol NaOH catalyst was chosen to fabricate capsuliform target. After 40 hours of the solution fabrication, the viscosity of the solution reaches 9E-5 m²/s which is proper to obtain capsule with shell less than 20 µm. By using PF solution with the above mentioned viscosity in O₉/O/W/O₁ emulsion process, the minimum gel shell thickness obtained was 17µm and (figure 2) while use RF the thickness was usually 50-100µm before drying. The fabrication condition was shown as following: the flowrate of W, O₁ and O₀ liquid were 0.083 mL/min, 0.130 mL/min and 93 mL/min, respectively.

Low polymer concentration of the precursory solution leads to low density of final dried gel. It was found that as the lower the concentration of the precursory PF solution obtained under base-catalyst, the more difficult for the solution to gelate. When 5 g PF gel (concentration=110 mg/cm³) was dissolved into 10 mL pure water to form solution, it took nearly two months for this solution to gel again. Furthermore, another 6mL of NaOH (1mol/L) has to be added as catalyst to continue the reaction. When 6 mL 1mol/L NaOH was added into PF solution, the pH was adjusted to 11.3 and the final concentration of the solution was as low as 2.63%. Based on this concentration, the theoretical density of the gel should be 26.3 mg/cc. This is by now the lowest concentration that was found for the PF solution to gel. That is to say, under this concentration, it is difficult for the solution to become gel. This may be because the low concentration leads to long distance between two nucleation sites so that it is difficult to be linked to form network structure.

![Figure 1. The viscosity changes of solutions with different amount of catalyst NaOH in them. The gelation race is affected by the amount of catalyst used. The more base catalyst used, the shorter time needed for gelation.](image1)

![Figure 2. By using PF as the shell material, the minimum shell thickness of the capsule fabricated by O₁/W/O₀ emulsion process was 17µm.](image2)
3.4. Microscopic morphology of the PF foam shell
The gel-shell capsule was CO₂ supercritical extracted to form porous structure for fuel support. The nano porous structure can be seen from the SEM image in figure 3. Pores of 100 nm can minimum the light scanning so that the final dried gel shell was transparent which is helpful to observe the fuel layer formation.

4. Conclusion
Phloroglucinolcarboxylic acid had addition and condensation reactions with formaldehyde in the presence of base catalyst and formed linear polymers. Therefore, the gelation rate and gelation concentration of the precursory PF solution was able to be controlled by different type and amount of catalyst used in the polymerization. By changing the type and amount of catalyst, the lowest concentration of PF polymer needed for gelation was 26.3 mg/cm³ and proper solution viscosity of 9E-5 was obtained for 16µm thick shell fabrication. The SEM of PF dried gel show fine porous structure which is available for fuel stock in fusion technique.

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