# Supporting Information

# Partially-methylated amyloses as effective hosts for inclusion complex formation with polymeric guests

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## 1. Synthetic procedures and monomer compositions of partially 2,3-*O*-methylated amyloses (MAs)

6-*O*-Triphenylmethyl-amylose was prepared by the reaction of amylose ($M_w$ = 2.1 x $10^4$, $M_w/M_n$ = 1.05) with triphenylmethyl chloride in pyridine, according to the previously reported method.[10] 6-*O*-Triphenylmethyl-amylose (1.2 g, 2.2 x $10^{-2}$ mmol, 3.0 mmol per monomer unit) was dissolved in dry THF (20 mL) under a $N_2$ atmosphere. NaH (0.083 ~ 2.0 mol per mol of OH) was then added to this solution. The suspension was stirred at ambient temperature for 1 h, and methyl iodide (2.6 g, 1.8 x $10^{-2}$ mol) was added. The mixture was then stirred at ambient temperature overnight. After the addition of methanol, the formed precipitate was separated, washed with methanol, and dried *in vacuo* to yield 2,3-*O*-methylated 6-*O*-triphenylmethyl-amylose as a yellow solid. 2,3-*O*-methylated 6-*O*-triphenylmethyl-amylose was dissolved in THF (40 mL). A 0.2 M HCl methanol solution (40 mL) was then added to this solution. The mixture was stirred at ambient

temperature for 2 days. After neutralization with an aqueous $Na_2CO_3$ solution, the solvent was removed *in vacuo*. The obtained solid was washed with THF, and dialyzed for 2 days against high purity (Millipore) water (molecular-weight cut-off of the dialysis film: 3,500 Da) to yield 2,3-*O*-methylated amylose (MA).

The degree of methylation of the MAs thus obtained was determined by trimethylsilylation of the unreacted OH groups, followed by an estimation of integral ratio of trimethylsilyl protons to the C-1 protons of the MAs based on their $^1$H NMR spectra. The trimethylsilylation of MA was carried out by stirring MA (10 mg) in pyridine (0.4 mL) with trimethylsilyl chloride in *n*-hexane (3 M solution, 0.31 mL) at ambient temperature overnight. The mixture was washed three times with brine (10 mL) and dried over anhydrous $MgSO_4$. After the filtration, the solvent was removed *in vacuo*. The obtained solid was dissolved in *n*-hexane (0.1 mL) and reprecipitated with methanol.

As a typical example, $^1$H NMR spectrum of trimethylsilylated MA-8 is shown in Fig. S1.

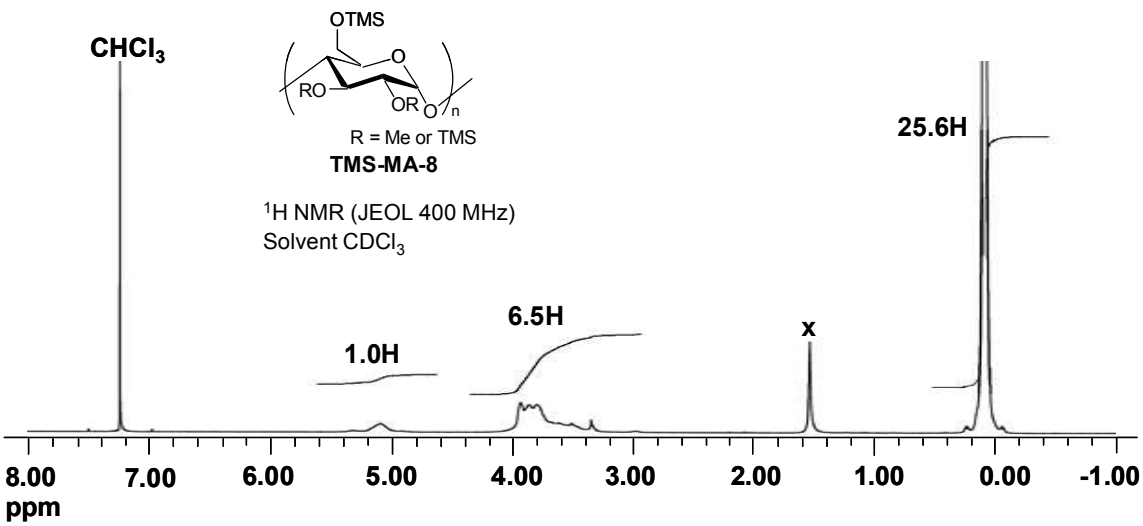


**Fig. S1** $^1$H NMR spectrum of trimethylsilylated MA-8 (in $CDCl_3$).

The monomer compositions of MAs were determined by HPLC analysis of the monomers obtained by the hydrolysis of MAs with 2 M trifluoroacetic acid (3 h, 100 °C). HPLC analysis was performed on an Sugar-D column (4.6 × 250 mm, Nacalai Tesque) at 20 °C, eluted with acetonitrile/$H_2O$ (75/25) at a flow rate of 1 mL/min and RI detection. The monomer compositions of MAs are shown in Table S1.

**Table S1** Monomer compostions[a] of MAs

| Host | D-Glucose | 2-*O* -Methyl- and/or 3-*O* -methyl-D-glucose[b] | 2,3-Di-*O* -methyl-D-glucose |
|---|---|---|---|
| MA-8 | 87 | 12 | 1 |
| MA-20 | 67 | 28 | 5 |
| MA-33 | 44 | 45 | 11 |
| MA-50 | 21 | 59 | 20 |
| MA-100 | 0 | 0 | 100 |

[a] Monomer compositions are expressed in molar percentages.
[b] Separation of 2-*O* -methyl-D-glucose and 3-*O* -methyl-D-glucose was not possible.

## 2. XRD patterns and $^1$H NMR spectra of precipitates between MAs and PTHF (or PCL)

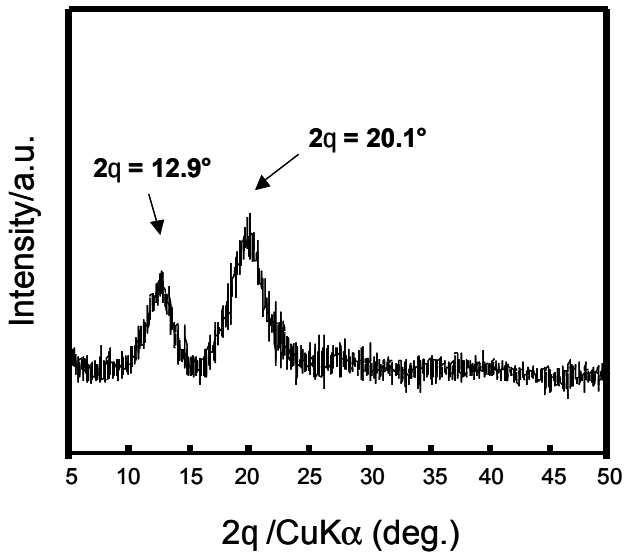


**Fig. S2** XRD patterns of the MA-20–PTHF precipitate.

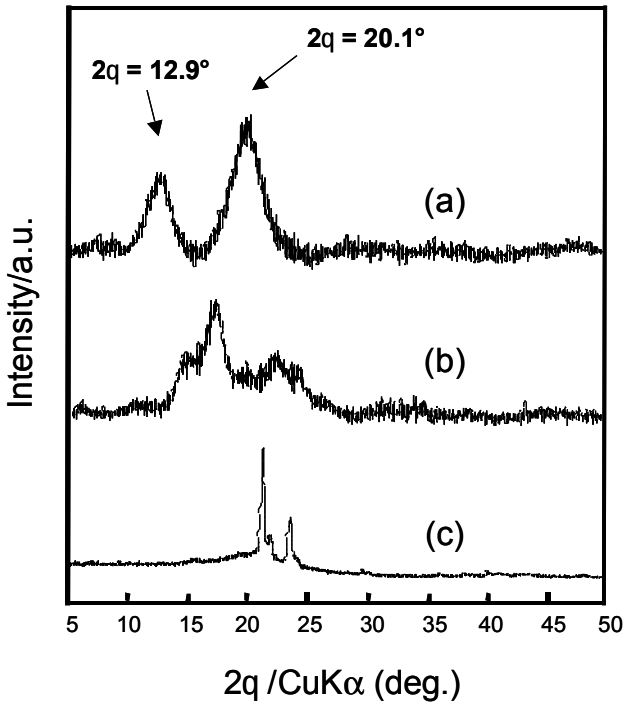


**Fig. S3** XRD patterns of (a) the MA-8–PCL precipitate, (b) MA-8 and (c) PCL.

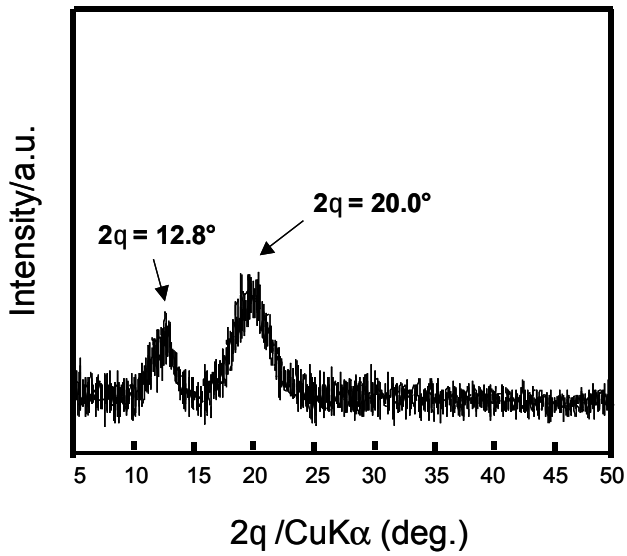


**Fig. S4** XRD patterns of the MA-20–PCL precipitate.

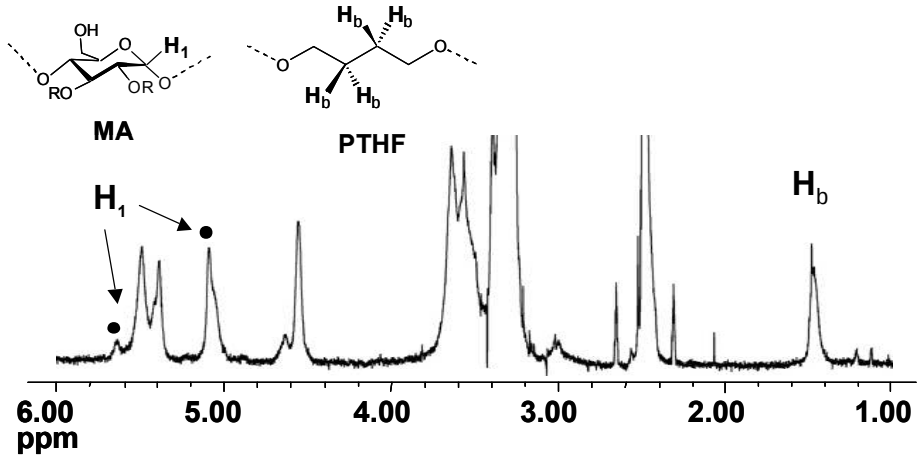


**Fig. S5** $^{1}$H NMR spectrum of the MA-20–PTHF precipitate (in DMSO-$d_6$).

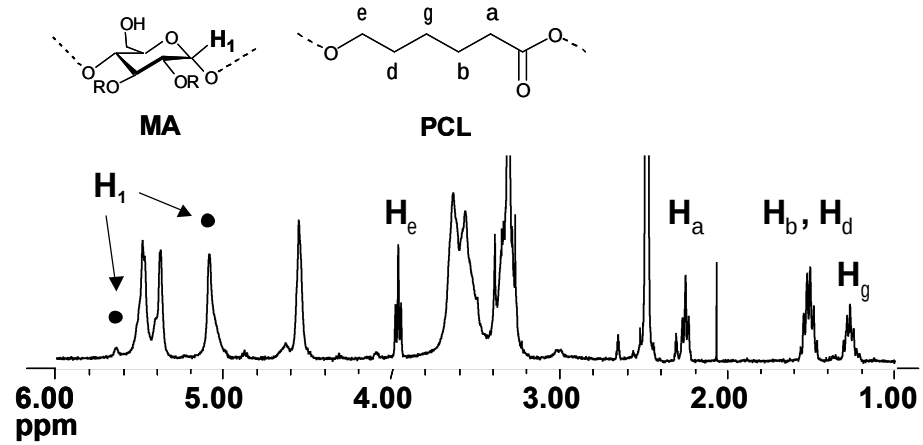


**Fig. S6** $^{1}$H NMR spectrum of the MA-8–PCL precipitate (in DMSO-$d_6$).

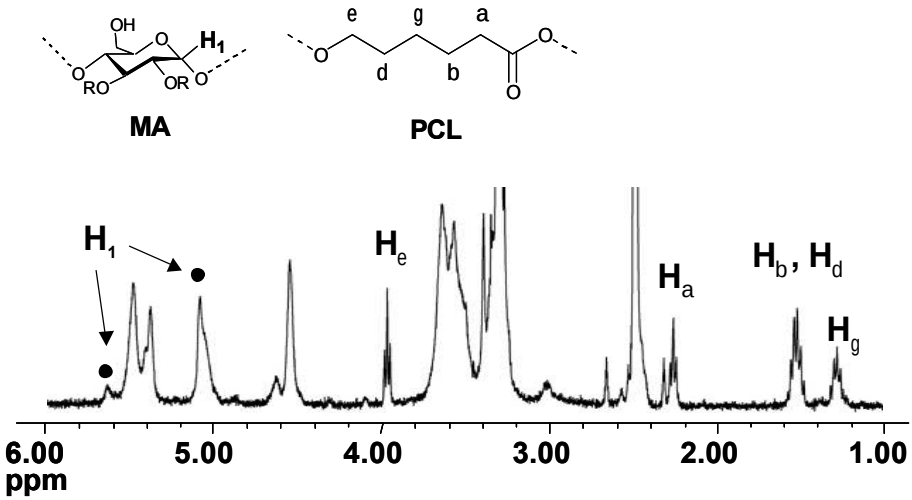


**Fig. S7** $^{1}$H NMR spectrum of the MA-20–PCL precipitate (in DMSO-$d_6$).

## 3. DSC thermograms of the precipitate between MA-8 and PCL

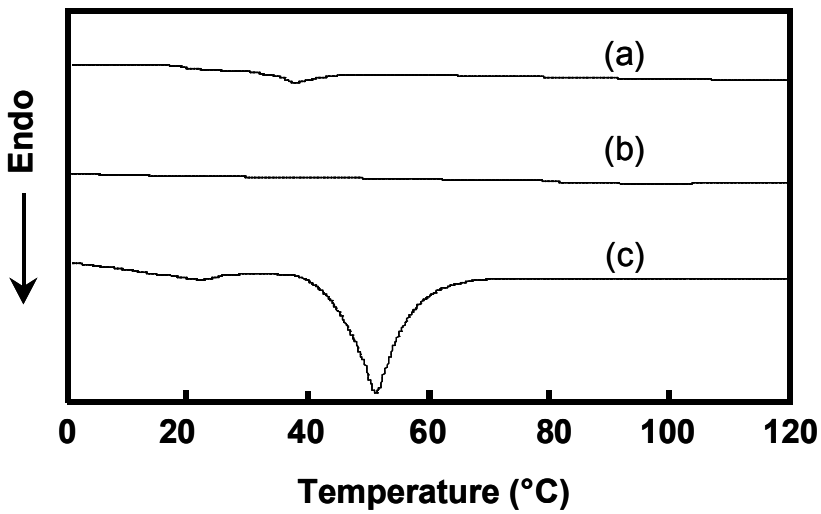


**Fig. S8** DSC thermograms (first heating scan at 10 °C/min) of (a) the MA-8–PCL precipitate, (b) MA-8 and (c) PCL.

## 4. XRD patterns and $^{1}$H NMR spectra of precipitates between amylose and PTHF (or PCL)

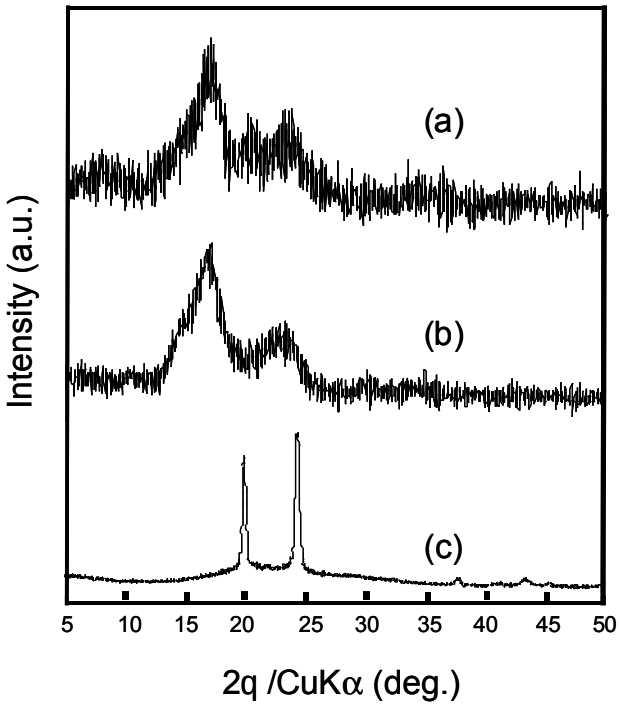


**Fig. S9** XRD patterns of (a) the amylose–PTHF precipitate, (b) amylose and (c) PTHF.

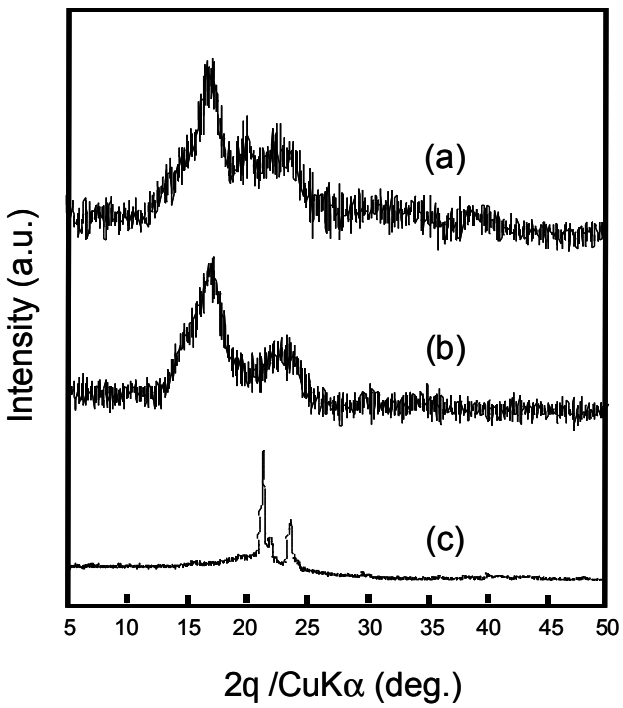


**Fig. S10** XRD patterns of (a) the amylose–PCL precipitate, (b) amylose and (c) PCL.

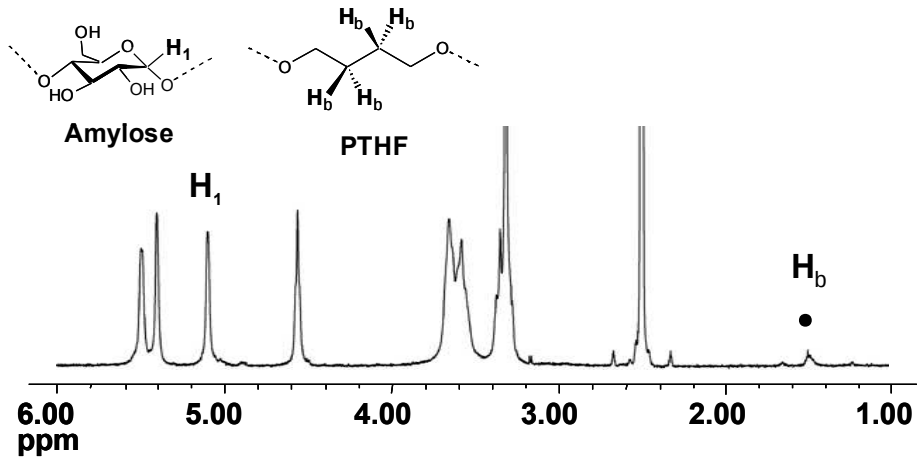


**Fig. S11** $^{1}$H NMR spectrum of the amylose–PTHF precipitate.

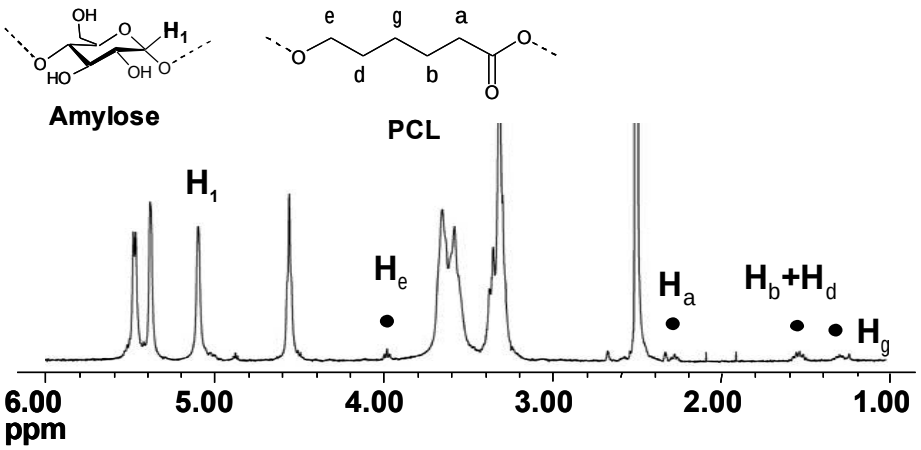


**Fig. S12** $^{1}$H NMR spectrum of amylose–PCL precipitate.