Formation of Supramolecular Soft Materials from Amylosic Inclusion Complexes with Designed Guest Polymers Obtained by Vine-Twining Polymerization

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ABSTRACT: Amylose forms supramolecular inclusion complexes with polymeric guests in the phosphorylase-catalyzed enzymatic polymerization field, so-called “vine-twining polymerization”. However, such inclusion complexes have not exhibited specific properties and processability as functional supramolecular materials. In this study, we found that amylosic inclusion complexes, which were obtained by vine-twining polymerization using a designed guest polymer, that is, an amphiphilic triblock copolymer poly(2-methyl-2-oxazoline-block-tetrahydrofuran-block-2-methyl-2-oxazoline), exhibited gel and film formation properties. The characterization results of the products suggested that enzymatically elongated amylose chains complexed with the polytetrahydrofuran block in the triblock copolymer. Accordingly, the outer poly(2-methyl-2-oxazoline) blocks constructed hydrophilic spaces among the inclusion complex segments. Furthermore, the presence of such outer blocks affected the lower regularity of crystalline alignment among the inclusion complex segments in the products. Such higher-order structures probably induced the formation of supramolecular soft materials, such as gels and films.

INTRODUCTION

Polysaccharides are one of the major classes of biopolymers and have been used as fundamental materials in traditional applications such as foods, cosmetics, pharmaceutical, and textile industries. Amylose is an energy polysaccharide as one component of starch and also known as a functional polymeric material owing to its left-handed helical conformation, composed of α(1→4)-linked glucose (G) repeating units. Because of hydrophobicity inside a cavity of the amylose helix, it can bind hydrophobic guest molecules with appropriate sizes, mostly monomeric molecules by hydrophobic interaction, to form amylosic supramolecules comprising the structure of inclusion complexes, so-called V-amylose. Polymeric guest molecules with high molecular weights are promising candidates to imply practical applications as supramolecular materials by complexation with amylose, compared to such monomeric guests. However, a limited number of studies have successfully investigated the direct complexation of amylose and polymeric guest molecules. Because weak hydrophobic interaction is a driving force for the incorporation of guest molecules into the amylose cavity, amylose is considered to be not having the ability to encapsulate long polymeric guests into its cavity. The introduction of suitable hydrophilic groups at the polymer chain ends has implied enhancement of the complexation in aqueous media to achieve the direct incorporation of polymeric guests into the cavity of amylose. The exchange from small guest molecules to large (polymeric) ones was also attempted to obtain amylose–polymer inclusion complexes. The inclusion polymerization approach has been achieved to directly form amylose–polymer inclusion complexes. Furthermore, the direct mixing approach under the selected conditions has been conducted to form an inclusion complex from amylose and poly(tetrahydrofuran) (PTHF). We have previously employed phosphorylase-catalyzed enzymatic polymerization as the dynamic field to form amylose–polymer inclusion complexes in situ. This enzymatic polymerization occurs by using α-D-glucose 1-phosphate (G-1-P) as a monomer, which is initiated from the chain end of a maltooligosaccharide primer. The propagation progresses with the formation of an α(1→4)-glycosidic linkage, according to the following reversible reaction: 

\[
\text{G-1-P} + \text{P(OMe)}_{2}\text{-THF-block-MeOx} \rightleftharpoons \text{G-1-P} + \text{Pi (inorganic phosphate)}
\]

When guest polymers with moderate hydrophobicity are dispersed in the aqueous enzymatic polymerization system, the propagation has been found to progress with binding the guest polymers in the cavity, giving rise to amylose–polymer inclusion complexes. In this system, the sufficient dynamic field for the more efficient complexation with polymeric guests than the direct complexation is provided during the enzymatic elongation from the short maltooligosaccharide primer to the longer amylose to form the inclusion complexes.

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complexes. The image of propagation in this system is similar to the way that the vines of plants grow with twining around a rod. Accordingly, we have proposed that this polymerization method can be called “vine-twining polymerization” for the formation of amylose–polymer inclusion complexes. For example, a hydrophobic polyester, PTHF, acts as a guest polymer with moderate hydrophobicity in the vine-twining polymerization, giving rise to the efficient formation of an amylose–PTHF inclusion complex. Regardless of the guest polymers, however, all the inclusion complexes, obtained by the vine-twining polymerization, have showed powdery appearances and not exhibited specific properties and processability as functional supramolecular materials, such as soft material formation, probably due to the regular crystalline structure and insufficient mechanical properties of V-amylose.

To fabricate amylosic supramolecular soft materials comprising V-amylose segments, such as gels and films, by vine-twining polymerization, we have employed immobilized primers (maltoheptaose, G7) or guest polymers as graft chains, vine-twining polymerization, we have employed immobilized structure and insulation formation, probably due to the regular crystalline processability as functional supramolecular materials, such as soft material formation, probably due to the regular crystalline structure and insufficient mechanical properties of V-amylose.

In the present study, we have attempted to fabricate amylosic supramolecular soft materials from the vine-twining polymerization products by using appropriately designed guest polymers, besides the abovementioned immobilization approach. Consequently, we found that vine-twining polymerization using an amphiphilic triblock copolymer composed of an inner hydrophobic PTHF block and outer hydrophilic poly(2-methyl-2-oxazoline) (PMeOx) blocks (P(MeOx-block-THF-block-MeOx)) provided the gel and film formation abilities in the resulting inclusion complexes (Figure 1). The characterization results suggested that the outer PMeOx chains constructed hydrophilic spaces among inclusion complex (V-amylose) segments with the inner PTHF chain and also contributed to lowering the regularity of crystalline alignment among the V-amylose segments, leading to new higher-order structures, suitable for the formation of supramolecular soft materials.

## RESULTS AND DISCUSSION

The guest triblock copolymers, (P(MeOx-block-THF-block-MeOx)s), with different compositional ratios were synthesized by ring-opening block copolymerization of THF with MeOx initiated by trifluoromethanesulfonic anhydride (Tf2O), according to a literature procedure. After acetylation of the terminal hydroxy groups were conducted using acetic anhydride in pyridine, the 

![Image](image1.png)

**Figure 1.** Vine-twining polymerization using P(MeOx-block-THF-block-MeOx) as the guest polymer.
amylose–PTHF inclusion complex produced by the same experimental manner using PTHF as the guest polymer. The XRD profiles of all of the products from the triblock copolymers show two typical diffraction peaks at around 13° and 20° corresponding to the distance between the helix centers (corresponding to approximately a diameter) and the helical pitch in the inclusion complex (Figure 2c–e),36 which are identical to the pattern of the inclusion complex from PTHF (Figure 2b) and from other slender guest polymers regardless of the DPs of amyloses as shown in previous studies25,26,37 but completely different from that of pure amylose (Figure 2a). These XRD profiles suggested that the inclusion complexes were formed in the present system using the amphiphilic triblock copolymers. Furthermore, the results also indicated the inclusion toward the PTHF blocks by amylose with exclusion of complexation with the PMeOx blocks in the triblock copolymers, owing to the former hydrophobicity and the latter hydrophilicity.

The 1H NMR results of the products from the triblock copolymers in DMSO-d6 also support the formation of the inclusion complexes because of the detection of both the signals assigned to amylose and the PTHF and PMeOx protons as shown in Figure 3. The inclusion ratios of the amylose cavities to the THF blocks were evaluated by the integrated ratio of the H1 (αanomeric) signals of the G residues to the methylene signals a (−C=CH2CH2−C−) of PTHF blocks (H1/a) in the 1H NMR spectra according to the calculation method reported in our previous literature on vine-twining polymerization using PTHF.26,38 Generally, one helical turn of amylose is composed of approximately six repeating G units when linear molecules of small cross-sectional area, such as PTHF, are included.39 A repeat distance of the amylose helix and a unit length of PTHF have been calculated to be 0.80 and 0.60 nm, respectively. Therefore, an average of 4.5 repeating G units in amylose corresponds to a unit length of...
From these calculations, the integrated ratio of the above H1 signals to the methylene signals (H1/a) in the 1H NMR spectrum is theoretically 1.13. The H1/a value in the 1H NMR spectrum of the amylose−PTHF inclusion complex (run 1) was calculated to be 0.9 (Figure 3a), which indicated that the amylose cavity included most (ca. 80%) of the PTHF chain. By the same calculation, the H1/a values in the 1H NMR spectra of the products of runs 2−4 (Figure 3b−d) were calculated to be 0.73, 0.66, and 0.56, which in turn indicated the inclusion of ca. 65, 58, and 49% of the PTHF chains by the amylose cavity (Table 1). These results suggested that the inclusion ratios of the amylose cavities to the PTHF blocks in the triblock copolymers decreased in accordance with the increase of hydrophilicities of the guest copolymers. This is because the driving force for the formation of inclusion complexes by amylose is a hydrophobic interaction, and accordingly, the longer PMeOx blocks present at both the ends of the PTHF block inhibit the complexation by amylose. The inclusion complexation on the PTHF blocks probably started by hydrophobic interaction with a short amylose and then progressed during its enzymatic chain-elongation to a longer amylose according to the vine-twining polymerization manner as our previous study already suggested.6 In addition to its hydrophilicity, furthermore, bulkiness of the PMeOx blocks is also considered to inhibit the complexation by amylose because vine-twining polymerization has been achieved mostly using slender guest polymers, such as PTHF without substituents on the main chain.6

Figure 3. 1H NMR spectra of (a−d) vine-twining polymerization products of runs 1−4 in DMSO-d6.

Dissociation of the inclusion complexes was conducted by the DMSO treatment according to our literature procedure.40 After solutions of the inclusion complexes in DMSO were maintained at 70 °C with stirring, the amylose and the guest polymer components were separated as fractions insoluble and soluble in methanol, respectively. The DP (Mn) values of the dissociated amyloses were determined from the λmax values in the UV–vis spectra of the violet solutions of complexes with iodine41,42 which decreased in accordance with the increase of the PMeOx block lengths (runs 2−4) with monomodal gel permeation chromatographic (GPC) profiles (Mw/Mn < 2.1) as shown in Table 1. The longer PMeOx blocks probably prevented the approach by the enzyme and thus the further enzymatic elongation of amylose chains helically present around the PTHF block, owing to steric hindrance of the PMeOx blocks. Similar prevention of the enzymatic elongation of amylose was also observed in another vine-twining polymerization system using G7-functionalized poly(l-lactide) (primer−guest conjugate).37 On the other hand, the DP values of the PTHF and PMeOx blocks in the dissociated guest copolymers were estimated from the 1H NMR results after acetylation of the terminal hydroxy groups by a similar manner to that mentioned above. In all cases, consequently, the DP values of the former blocks increased, whereas those of the latter blocks decreased compared with the values of the original triblock copolymers. These results suggested that the enzymatically elongated amylose chains preferentially included the more hydrophobic fractions distributed in the triblock copolymers. Indeed, the Mw/Mn values of the dissociated triblock copolymers, which were estimated by GPC analysis, were smaller than those of the original ones (Table 1), suggesting the inclusion of specific fractions in the original triblock copolymers by the amylose chains. Based on the Mn values of the amylose components and the DP values of the PTHF blocks in the guest polymer components, the inclusion ratios were calculated to be 62, 53, and 43% for runs 2−4, which were in good agreement with those estimated from the abovementioned integrated ratios in the 1H NMR spectra.

Figure 4. (a−d) Photographs of materials by treatments of products of runs 1−4 with methanol and subsequently water and (e−h) SEM images of lyophilized samples from the treated materials of runs 1−4.
According to the lengths of the amylose helixes and PTHF blocks, estimated from their DP (\(M_n\)) values (6.3–10.5 and 15.0–17.6 nm, respectively), it can be considered that one amylose chain includes averagely one or possibly two guest molecules.

As one of the potential new functions of the products, which can be applied as functional supramolecular materials, their swellability was investigated. Consequently, the products of runs 3 and 4 were facilely swollen in methanol with ultrasonication, while such swellability in methanol was not observed from the other two products (runs 1 and 2). Furthermore, when the resulting samples were immersed in water for 24 h to exchange disperse media, the former two swollen samples could be converted into hydrogels with water contents of 74.4 and 81.2%, respectively (Figure 4c,d), but the others remained intact as powder (Figure 4a,b). Additionally, pure P(MeOx-block-THF-block-MeOx) did not show swellability with methanol and water, but it was dissolved in methanol and suspended and then agglomerated in water. The frequency dependence of storage and loss modulus (\(G'\) and \(G''\), respectively) in the dynamic viscoelastic measurement of the hydrogel of run 3 shows the signature of the typical viscoelastic material with predominance of storage modulus in the whole frequency range (Figure 5), supporting the gelling state of this sample. To reveal the difference in swellabilities of the products of runs 1–4, their crystalline structures were evaluated by comparison of the XRD profiles of the lyophilized samples after the treatment experiment (Figure 6). The area ratios of two peaks, i.e., peak A at 13° to peak B at 20°, decrease in the order of runs 1–4. As these peaks were owing to the distance between the helix centers in the crystalline alignment among the inclusion complexes and the helical pitch of the amylose helix in the inclusion complex, respectively, the XRD results suggested that amylose chains formed regularly controlled helixes on the PTHF blocks regardless of the PMeOx block lengths, while regularity of the crystalline alignment among the complexes (V-amylose) decreased in accordance with the PMeOx block lengths. Accordingly, upon increasing the PMeOx block lengths, more hydrophilic spaces were formed among the aligned V-amylose packing assembly, compared with the amylose–PTHF inclusion complex as shown in Figure 7a,b, resulting in an ability to draw the highly polar media such as methanol and water for swelling. Peak A at 13° was detected in the XRD profiles, however, the inclusion complex segments still interacted, even in lower regularity, to act as cross-linking points for gelation. The scanning electron microscopic (SEM) images of the lyophilized samples from the hydrogels (runs 3 and 4) show porous structures representatively constructed from the cross-linked network structures (Figure 4g,h). On the other hand, such a porous morphology is not seen in the SEM images of the lyophilized samples from any materials of runs 1 and 2 without gelation (Figure 4e,f).

When DMSO solutions of the products were casted on a glass plate, followed by drying, the samples of runs 3 and 4 with the longer PMeOx chains formed transparent films (Figure 8c,d), whereas the film formation was not observed with the other samples (runs 1 and 2, Figure 8a,b). The XRD results of the resulting films exhibit the patterns assignable to the inclusion complexes (Figure 2h,i), whereas such patterns are not obviously detected in those of the other samples (Figure 2f,g). These results suggested that the longer PMeOx blocks present at both ends of the PTHF blocks were affected to prevent the dissociation of the complexes in DMSO during the film formation procedure. In addition to such a stabilization effect by the longer PMeOx chains, the lowered regularity of crystalline alignment among the inclusion complex segments in the products of runs 3 and 4 contributed to providing the film formation properties.
**CONCLUSIONS**

In this study, we investigated vine-twining polymerization using the designed amphiphilic triblock copolymer, that is, P(MeOx-block-THF-block-MeOx). The amylose chains specifically included the PTHF block in the triblock copolymer to form the inclusion complex having the nonincluded PMeOx chains at both sides. Accordingly, the PMeOx chains formed hydrophilic spaces among the inclusion complex segments, in which their regularity of crystalline alignment was also lowered. Owing to such higher-order structures, the amylosic supramolecular products formed soft materials, such as gels and films. The present approach opens up a new way to provide functions in the amylosic supramolecular inclusion complex. Furthermore, the resulting supramolecular soft materials in this study have potential to be employed in practical applications such as biomedical and environmentally benign fields in the future.

**EXPERIMENTAL SECTION**

**Materials.** MeOx was prepared from acetonitrile and 2-aminoethanol in the presence of zinc acetate according to the literature procedure and purified by distillation.\(^4^4\) Tf\(_2\)O was prepared by dehydration of phosphorus pentoxide and purified by distillation. PTHF was prepared by ring-opening polymerization of THF in the presence of EtOTf according to a literature procedure (\(M_n = 1890\) by \(^1\)H NMR).\(^35\) Thermostable phosphorylase from Aquifex aeolicus VFS was supplied from Ezaki Glico Co. Ltd., Osaka, Japan.\(^24,45,46\)

**Synthesis of P(MeOx-block-THF-block-MeOx).**\(^34\) A typical experimental procedure was as follows (run 2). A mixture of G-1-P (0.152 g, 0.50 mmol), G\(_7\) (5.8 mg, 5.0 \(\mu\)mol), and P(MeOx-block-THF-block-MeOx) (\(M_n = 2560\), 0.256 g, 0.10 mmol) in sodium acetate buffer (pH = 6.2, 0.2 mol/L, 7.5 mL) was ultrasonicated for 2 h to obtain a dispersion. After addition of the thermostable phosphorylase (90 U), the mixture was stirred at 40 °C for 24 h. The precipitate was then filtered, washed with water and methanol, and dried under reduced pressure to give the inclusion complex (56.5 mg).\(^1\)H NMR (DMSO–d\(_6\)) \(\delta\) 1.49 (br, –CH\(_3\) of PMeOx), 3.33–3.64 (m, –CH\(_2\)O of PTHF, –CH\(_2\)N of PMeOx, H\(_2\)-H\(_6\) of amylose, overlapping with HOD), 5.09 (br, H\(_1\)), 4.56, 5.39, 5.48 (OH of amylose).

**Dissociation of Inclusion Complexes.** A typical experimental procedure was as follows (run 2). A mixture of the inclusion complex (40.0 mg) with DMSO (1.0 mL) was heated at 70 °C for 1 h with stirring for dissolution. The resulting solution was poured into methanol (50 mL) to precipitate amylose, which was isolated by filtration, washed with methanol, and dried under reduced pressure (23.9 mg). The filtrate was concentrated to obtain the guest copolymer (8.0 mg).

The \(M_n\) value of the dissociated amylose was determined by UV–vis analysis of the complex with iodine.\(^41,42\) A standard iodine–iodide solution was first prepared by dissolving potassium iodide (5.2 mg, 0.031 mmol) and iodine (5.2 mg, 0.020 mmol) in water (10 mL). The amyllose sample (1.0 mg) was dissolved in DMSO (0.20 mL) and the standard iodine–iodide solution (1.0 mL) was added to the solution. The violet solution was then characterized by UV–vis spectroscopy to determine the \(M_n\) value; \(\lambda_{max} = 594.0 \text{ nm, } M_n = 13250\).

**Formation of the Hydrogel.** After a mixture of the inclusion complex (25.0 mg) with methanol (30 mL) was ultrasonicated for 2 h and centrifuged, the supernatant was decanted off. The paste-like swollen material was soaked in...
water (30 mL) for 24 h to obtain the hydrogel. The water content was calculated by weight difference between the hydrogel and its lyophilized sample. A mixture of the dissociated guest copolymer (4.0 mg), acety halide (1.0 mL), and pyridine (1.0 mL) was stirred at room temperature overnight. The reaction mixture was then poured into hexane (50 mL) to precipitate the product, which was isolated by centrifugation and dried under reduced pressure to give an acetyl-terminated copolymer (3.1 mg). $^1$H NMR (DMSO-$d_6$) δ 4.14–4.27 (br, –CH$_2$O(C=O)CH$_3$ (terminal acetate methylene)). From the integrated ratio of this signal to a methylene signal of the PTHF block (–C–CH$_2$–C–) at δ 1.61 and a methyl signal of the PMeOx block at δ 2.11, the DP values of PTHF and PMeOx blocks were calculated to be 29.3 and 9.2, respectively.

**Formation of the Film.** The inclusion complex (10.0 mg) was dissolved in DMSO (0.10 mL) by heating at 70 °C for 10 min with stirring. The resulting solution was casted on a glass plate and dried under reduced pressure at 70 °C for 2 h to obtain the film.

**Measurements.** $^1$H NMR spectra were recorded on a JEOL ECA600 spectrometer. XRD measurements were performed using a PANalytical X’Pert Pro MPD diffractometer with Ni-filtered Cu Kα radiation (λ = 0.15418 nm). UV–vis measurements were conducted using a Jasco V-650 spectrometer. GPC analysis was performed by using a pump NPL-5000 (Nihon Seimitsu Kagaku, Co. Ltd.) and a TOSOH NPL-5000 (Nihon Seimitsu Kagaku, Co. Ltd.) and a TOSOH GPC LF-804 column with DMSO as the eluent at a flow rate of 0.3 mL/min at room temperature. Pullulan samples were measured using a Jasco V-650 spectrometer. GPC analysis was performed by using a pump NPL-5000 (Nihon Seimitsu Kagaku, Co. Ltd.) and a TOSOH NPL-5000 (Nihon Seimitsu Kagaku, Co. Ltd.) and a TOSOH GPC LF-804 column with DMSO as the eluent at a flow rate of 0.3 mL/min at room temperature. Pullulan samples were measured using a Jasco V-650 spectrometer.

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**Notes**

The authors declare no competing financial interest.

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