Polym. Bull. (2009) 62:291–303
DOI 10.1007/s00289-008-0025-8

ORIGINAL PAPER

Chemoenzymatic synthesis of amylose-grafted polyacetylene by polymer reaction manner and its conversion into organogel with DMSO by cross-linking

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Received: 13 October 2008 / Revised: 12 November 2008 / Accepted: 30 November 2008 /
Published online: 10 December 2008

Abstract This paper reports chemoenzymatic synthesis of amylose-grafted polyacetylene according to the following polymer reaction manner. At first, the amine-functionalized polyacetylene was prepared by the Rh-catalyzed copolymerization of a protected amine-substituted acetylene monomer (*tert*-butyl propargylcarbamate) with *N*-propargylethanamide, followed by deprotection process. Then, the maltooligosaccharide chains were introduced on the polyacetylene by the reaction with maltoheptaose lactone. Finally, the phosphorylase-catalyzed enzymatic polymerization from the oligosaccharides on the produced polyacetylene was performed using α-D-glucose 1-phosphate as a monomer to give the polyacetylene having amylose graft-chains. Furthermore, the cross-linking reaction of the remaining amino-groups on the amylose-grafted polyacetylene with hexamethylene diisocyanate was carried out in DMSO to give the insoluble material, which formed the organogel with DMSO. The mechanical property of the gel was evaluated by compressive stress–strain measurement.

Keywords Chemoenzymatic · Amylose · Polyacetylene · Polymer reaction · Cross-linking · Organogel

Introduction

Researches concerning conjugated polymers, such as polyacetylene, polypyrrole, and polyphenylene, have attracted much attention in terms of the various practical applications of their interesting electrical and optical properties [1, 2]. Moreover,

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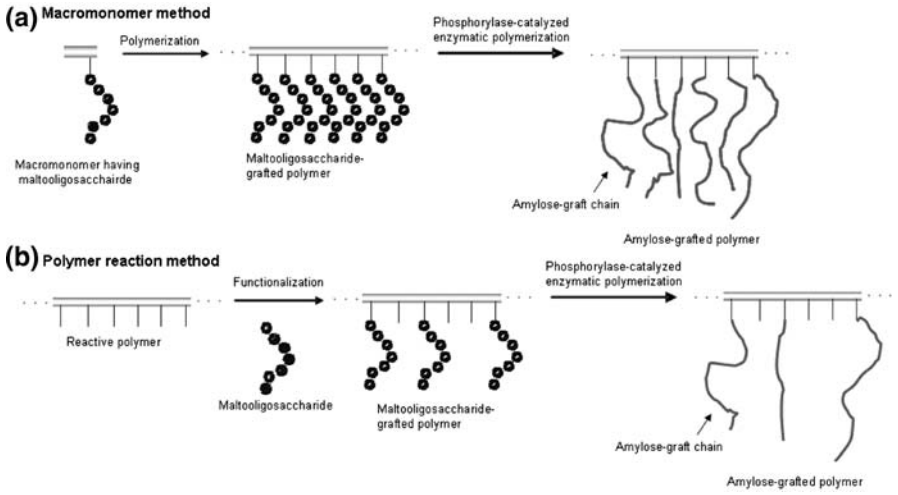
interests and applications of the conjugated polymers have been extended to the biological fields. In order to endow the conjugated polymers with the biological functions derived from sugar residues, for example, the sugar-substituted conjugated polymers were synthesized by using the conjugated main-chain structures of polyaniline [3], polyisocyanide [4], polythiophene [5], poly(*p*-phenylene) [6, 7], poly(*p*-phenylene ethynylene) [8], and poly(*p*-phenylene vinylene) [9]. In the series of these studies, we have reported the synthesis of poly(*N*-propargylamide)s with galactose residues [10, 11]. They contained the *cis*-polyacetylene main-chains and were obtained by the Rh-catalyzed polymerization of the corresponding *N*-propargylamide monomers.

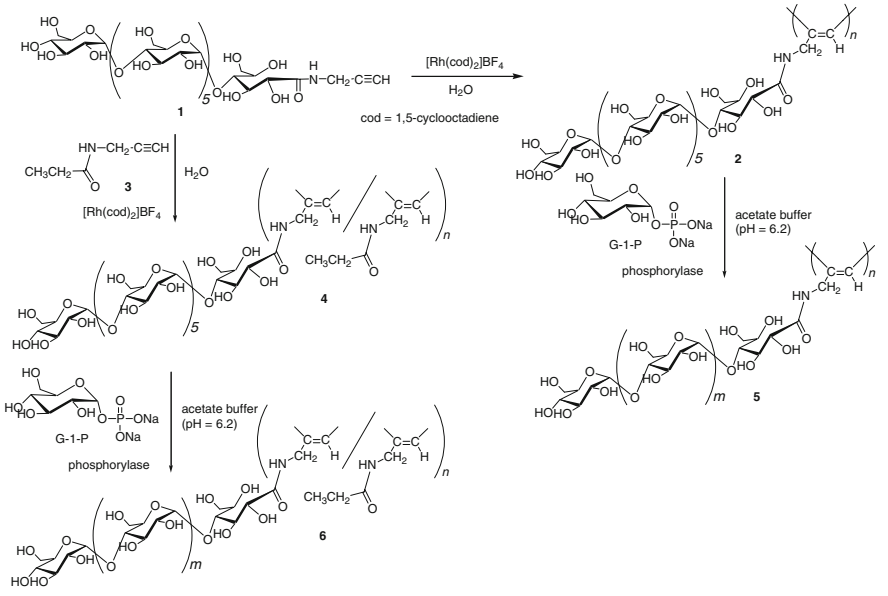
On the other hand, the glycopolymers grafting the saccharide chains with the higher degree of polymerization (DP), e.g., polysaccharides, are interesting because this type of the polymers would exhibit the hybrid properties of synthetic polymer and polysaccharide. In the previous studies on the synthesis of such the polysaccharide-grafted polymers, the enzymatic polymerization has been employed because this type of polymerization is a very powerful tool to obtain polysaccharides with well-defined structure [12, 13]. For example, the phosphorylase-catalyzed enzymatic polymerization using α-D-glucose 1-phosphate (G-1-P) as a monomer has been used, which proceeds with the regio- and stereoselective construction of α-glycosidic bond under mild conditions, leading to the direct formation of (1 → 4)-α-glucan chain, i.e., amylose, in the aqueous media [14]. This polymerization is initiated from a maltooligosaccharide primer like maltoheptaose. Then, the propagation proceeds through the following reversible reaction to produce amylose; $((\alpha, 1 \rightarrow 4)\text{–G})_n$ + G-1-P ⇄ $((\alpha, 1 \rightarrow 4)\text{–G})_{n+1}$ + P. In the reaction, a glucose unit is transferred from G-1-P to the nonreducing 4-OH terminus of a (1 → 4)-α-glucan chain, resulting in inorganic phosphate (P).

This enzymatic polymerization has been combined with the appropriate chemical reaction (chemoenzymatic method) to produce the polymers having the amylose graft-chains. For example, the amylose-grafted polystyrenes were prepared according to the synthetic manner of '*macromonomer method*' as shown in Scheme 1a [15, 16], in which the maltooligosaccharide-grafted polystyrenes were first prepared by the polymerization of the corresponding macromonomers having the maltooligosaccharide substituents, and then, the phosphorylase-catalyzed polymerization using G-1-P from non-reducing ends of the oligosaccharide side-chains on the polystyrene main-chains was performed. The other efficient synthetic manner according to '*polymer reaction method*' (Scheme 1b) has also been performed for the chemoenzymatic synthesis of the amylose-grafted polymers. In this manner, the maltooligosaccharide chains were first introduced on the main-chains of the desired reactive polymers. Then, the phosphorylase-catalyzed enzymatic polymerization was carried out using the product and G-1-P to give the amylose-grafted polymers. The previous studies have efficiently employed this type of approach to obtain the amylose-grafted polysiloxanes [17–20], poly(L-glutamic acid) [21], and chitin/chitosan [22, 23].

In our previous paper, we applied the macromonomer method to the chemoenzymatic synthesis of the amylose-grafted polyacetylenes (Scheme 2) [24]. At first, Rh-catalyzed polymerization of a *N*-propargylamide-type macromonomer **1** having an maltooligosaccharide substituent was carried out to give the polyacetylene **2** with

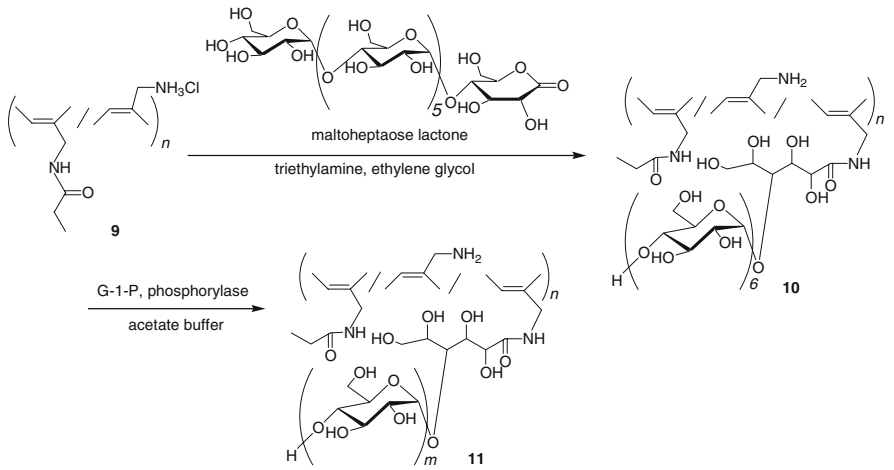


Scheme 1 Two approaches for chemoenzymatic synthesis of amylose-grafted polymers; macromonomer method (*a*) and polymer reaction method (*b*)



Scheme 2 Chemoenzymatic synthesis of amylose-grafted polyacetylenes by macromonomer method

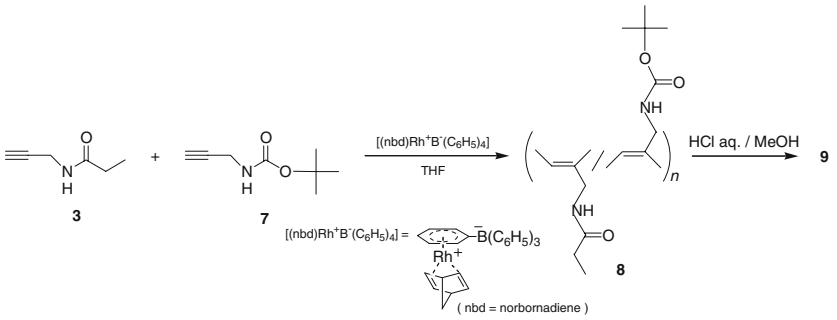
the pendant maltooligosaccharide chains. Then, the phosphorylase-catalyzed enzymatic polymerization of **2** using G-1-P was performed to produce the desired amylose-grafted polyacetylene **5**. The enzymatic polymerization of the copolymer **4** which was obtained by the copolymerization of **1** with the other *N*-propargylamide



Scheme 3 Chemoenzymatic synthesis of amylose-grafted polyacetylene by polymer reaction method

monomer **3** was also conducted to yield **6**. However, the DPs of the obtained polymers were not high (ca. 10), probably due to steric hindrance of the bulky oligosaccharide chains in the monomer and the polymers.

To obtain the amylose-grafted polyacetylene with the higher DP, in this study, we designed the alternative approach according to the polymer reaction method (Scheme 3). We first prepared the amine-functionalized polyacetylene **9** with the high DP according to Scheme 4, which had the ability to react with maltoheptaose lactone, giving the maltooligosaccharide-grafted polyacetylene **10**. Then, the phosphorylase-catalyzed polymerization from the maltooligosaccharide chains on **10** produced the desired amylose-grafted polyacetylene **11**. To evaluate a possibility for the practical application of **11** as the new hybrid material of polyacetylene with amylose for the future study, furthermore, the cross-linking reaction of the remaining amino-groups on **11** with hexamethylene diisocyanate was carried out in DMSO to give the easily handled organogel **12**. The mechanical property of the gel was evaluated by compressive stress–strain measurement.



Scheme 4 Synthesis of amine-functionalized polyacetylene **9** by copolymerization of **3** with **7**, followed by deprotection

Experimental

Materials

Maltoheptaose lactone was prepared from maltoheptaose according to the literature procedure [18]. Phosphorylase (300 U/mL) was supplied by Ezaki Glico Co. Ltd [25]. *N*-propargylethanamide (**3**) and (nbd)$Rh^+B^-(C_6H_5)_4$ were prepared according to the literature procedures [26, 27]. Other reagents and solvents were used as received.

Synthesis of *tert*-butyl propargylcarbamate **7**

Under argon, di-*tert*-butyl dicarbonate (1.637 g, 7.50 mmol) was added to a mixture of propargylamine hydrochloride (0.458 g, 5.00 mmol) and triethylamine (1.40 mL, 10.0 mmol) in acetonitrile (15.0 mL) at room temperature and the resulting mixture was stirred at that temperature for 20 h. After the precipitated triethylammonium hydrochloride was filtered off, the filtrate was evaporated and dried under reduced pressure. The residual material was subject to column chromatography on silica gel (eluent; hexane/ethyl acetate = 20:1 v/v) to give **7** (0.726 g, 4.70 mmol) in 93.6% yield.

^{1}H NMR ($CDCl_3$): δ 1.47 (*s*, CH_3, 9H), 2.22 (*t*, $J = 2.5$ Hz, HC≡, 1H), 3.92 (*s*, CH_2–C≡, 2H), 4.70 (*s*, NH, 1H).

Typical procedure for copolymerization of **3** with **7**

A typical copolymerization procedure was as follows (entry 2, Table 1). Under argon, a solution of catalyst, (nbd)$Rh^+B^-(C_6H_5)_4$ (0.0923 g, 0.180 mmol) in THF (3.0 mL) was added to a solution of **3** (0.139 g, 1.25 mmol) and **7** (0.0839 g, 0.540 mmol) in THF (0.60 mL) and the mixture was stirred at 30 °C for 1 h. The resulting solution was poured into a large amount of diethyl ether to precipitate the polymeric product. The precipitate was isolated by filtration and dried under reduced pressure to give **8** (0.177 g, 1.46 mmol) in 81.6% yield.

^{1}H NMR ($CDCl_3$): δ 1.11 (CH_3 of ethyl), 1.41 (CH_3 of *tert*-butyl), 2.26 (CH_2 of ethyl), 3.82–4.00 (CH_2–C=), 6.09 (HC=), 7.74 (NH).

Deprotection of **8**

To a solution of **8** (0.160 g, 1.31 mmol, entry 2 in Table 1) in methanol (3.0 mL) was added 3.0 mol/L hydrochloric acid (6.0 mL) and the mixture was stirred at room temperature for 1 h. The reaction mixture was evaporated and the residue was dissolved in a small amount of methanol. Then, the solution was poured into a large amount of chloroform to precipitate the crude product, which was further treated with methanol. The insoluble fraction was filtered off and the filtrate was evaporated. The obtained material was dried under reduced pressure to give **9** (0.125 g, 1.17 mmol) in 89.3% yield.

^{1}H NMR (D_2O): δ 1.02 (CH_3), 2.19 (CH_2 of ethyl), 3.80 (CH_2–C=), 6.00 (HC=).

Table 1 Copolymerization of **3** with **7** and deprotection of **8**

Entry	Feed ratio	Yield[a]	Unit ratio[b]	GPC result of **8**[c]		Yield of **9**[d]
	3:**7**	(%)	**3**:**7**	M_n	M_w/M_n	(%)
1	0.9:0.1	96.7	0.92:0.08	7,800	1.8	84.1
2	0.7:0.3	81.6	0.76:0.24	11,900	1.8	89.3
3	0.5:0.5	99.0[e]	0.47:0.53	7,700	1.5	84.0

Solvent: THF, catalyst: (nbd)$Rh^+B^-(C_6H_5)_4$ (10 mol% for **3** + **7**), reaction temperature: 30 °C, reaction time: 1 h

[a] Fraction insoluble in diethyl ether

[b] Determined by ^{1}H NMR spectra

[c] Determined by GPC with 0.020 mol/L LiCl/DMF as the eluent using poly(ethylene glycol) standards

[d] Fraction insoluble in chloroform, which was purified further by treatment with methanol

[e] Fraction insoluble in a mixed solution of diethyl ether and hexane (1:1 v/v)

Synthesis of **10**

A typical experimental procedure was as follows. Under argon, a solution of maltoheptaose lactone (0.403 g, 0.350 mmol) in ethylene glycol (2.0 mL) was added to a solution of **9** (0.0614 g, 0.578 mmol) in ethylene glycol (0.50 mL) and the mixture was stirred at 70 °C for 21 h. After the reaction mixture was poured into acetone, the precipitate was dialyzed against water (molecular cut: 14,000) for 48 h. The obtained solution was evaporated and dried under reduced pressure to give **10** (0.0633 g, 0.408 mmol) in 70.6% yield.

^{1}H NMR (D_2O): δ 1.04 (CH_3), 2.20 (CH_2 of ethyl), 3.60–4.40 (CH_2–C= and sugar protons except anomeric protons), 5.11 and 5.33 (anomeric protons), 6.02–6.23 (HC=).

Enzymatic polymerization

As a typical experimental procedure, a solution of G-1-P (0.3042 g, 1.00 mmol) in aqueous 0.050 mol/L acetate buffer (5.0 mL) was added to a solution of **10** (0.0612 g, 0.394 mmol) in aqueous 0.050 mol/L acetate buffer (25 mL). The reaction was started by addition of phosphorylase (ca. 300 units) and the mixture was stirred at 40 °C for 24 h. After the reaction mixture was dialyzed against water (molecular cut: 14,000), a large amount of methanol was added to the obtained solution to precipitate the product. The precipitate was isolated by filtration, washed with water, and dried under reduced pressure to give **11** (0.200 g, 0.287 mmol) in 73.6% yield.

^{1}H NMR (1.0 mol/L NaOD/D_2O): δ 1.13 (CH_3), 2.22 (CH_2 of ethyl), 3.50–3.92 (CH_2–C= and sugar protons except anomeric protons), 5.26 (anomeric protons).

Gelation of **11** by reaction with hexamethylene diisocyanate

To a solution of **11** (0.103 g, 0.147 mmol) in DMSO (1.0 mL) was added hexamethylene diisocyanate (20.0 μL, 0.12 mmol) at room temperature. The

mixture was stirred at that temperature for 5 min, and then kept at 80 °C for 40 min. After the resulting product was further soaked in DMSO for 3 days, the obtained gelic material was taken out from DMSO solution and kept at room temperature for 5 days. Then, the surface of the gel was washed with methanol, followed by the dryness under ambient atmosphere to give the gel.

Measurements

NMR spectra were recorded on JEOL ECX 400 spectrometer. Gel permeation chromatography (GPC) analyses were performed using a Shimadzu LC-6A with RI detector under the following conditions: Shodex K-803 and K-804 columns with 0.020 mol/L LiCl/DMF as the eluent at a flow rate of 1.0 mL/min at 60 °C. The calibration curve was obtained using poly(ethylene glycol) standards.

Results and discussion

Preparation of amine-functionalized polyacetylene **9**

For the chemoenzymatic synthesis of amylose-grafted polyacetylene according to the polymer reaction manner as shown in Scheme 1b, the amine-functionalized polyacetylene is suitable as the starting reactive polymer, because the maltooligosaccharide chains can be grafted on the polyacetylene main-chain by the reaction of the amino group with the lactone derivative of maltooligosaccharide. However, the polymerizability of the acetylene monomer having a free amino group is not generally high, resulting in the polymer in low yield or with low DP. Therefore, we synthesized the protected amine-substituted acetylene monomer as the structure of **7**, in which the amino group in the monomer was protected by a *tert*-butoxycarbonyl (BOC) group. Thus, the amine-functionalized polyacetylene **9** is possibly obtained by the copolymerization of **3** with **7**, followed by the deprotection process (Scheme 4).

The copolymerization of **3** with **7** was performed under the standard conditions using a catalyst of $(nbd)Rh^{+}B^{-}(C_6H_5)_4$ in THF. The product was isolated as a fraction insoluble in diethyl ether or a mixed solution of diethyl ether and hexane (1:1 v/v) and the structure of the product was determined by the ^1H NMR spectrum. All the signals in the ^1H NMR spectrum ($CDCl_3$) were fully assignable to **8** as indicated in Fig. 1 (entry 2, Table 1), supporting the structure of the product as **8**. Specifically, the observation of a signal **e** ascribed to the main-chain protons of CH=C at around 6.09, which realistically corresponds to the *cis*-conformation, has indicated that the copolymerization proceeded to produce the polyacetylene with the main-chain of *cis*-isomer. Table 1 shows the selected results of the copolymerization. The unit ratios of **3** to **7** in the copolymers, determined by the integrated ratios of the signal **a** to the signal **b** in the ^1H NMR spectra, were in good agreement with the feed ratios of the monomers. The M_n values were estimated by GPC measurement with 0.020 mol/L LiCl/DMF as the eluent using the poly(ethylene glycol) standards to be 7,700–11,900, which correspond to the DPs of ca.72–112.

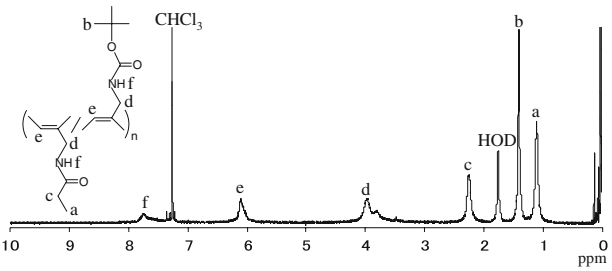


Fig. 1 ^{1}H NMR spectrum of **8** in $CDCl_3$

Because these values had been much larger than those of the polyacetylenes **2** and **4** (DPs = ca. 10) produced by the macromonomer method in our previous literature [24], **8** was suitably used for the following polymer reaction method as primary designed in this study (Scheme 3).

Consequently, the deprotection of **8** was carried out under the acidic conditions in a mixed solution of 3.0 mol/L hydrochloric acid/methanol. The products were isolated in the relative high yields as shown in Table 1, as fractions insoluble in chloroform, which were purified further by treatment with methanol. The ^{1}H NMR spectrum of the isolated copolymer in D_2O (Fig. 2, entry 2 in Table 1) exhibited no signals due to the methyl protons of BOC groups at the field pointed by an arrow. This indicated the occurrence of the complete deprotection, giving the amine-functionalized polyacetylene **9** as the hydrochloride form.

Synthesis of maltooligosaccharide-grafted polyacetylene **10**

Because the reaction of sugar lactone with amine had been known to proceed efficiently, the synthesis of maltooligosaccharide-grafted polyacetylene was performed by the reaction of maltoheptaose lactone with **9** under the appropriate conditions. The product was isolated as a fraction insoluble in acetone and purified further by the dialysis. The ^{1}H NMR spectrum of the product (D_2O) obtained using **9** of run 2 in Table 1 (Fig. 3) showed the signals **c**, **d**, and **e** due to the maltooligosaccharide, in addition to the signal **f** ascribed to the main-chain as well as the signals **a** and **b** assigned to the ethyl group, supporting the structure of the

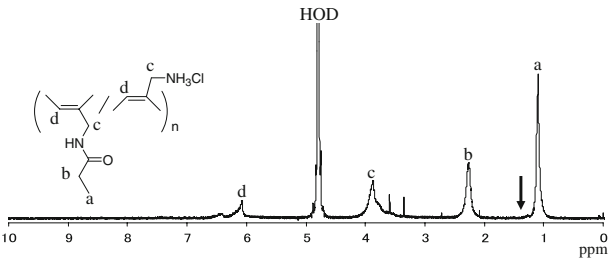


Fig. 2 ^{1}H NMR spectrum of **9** in D_2O

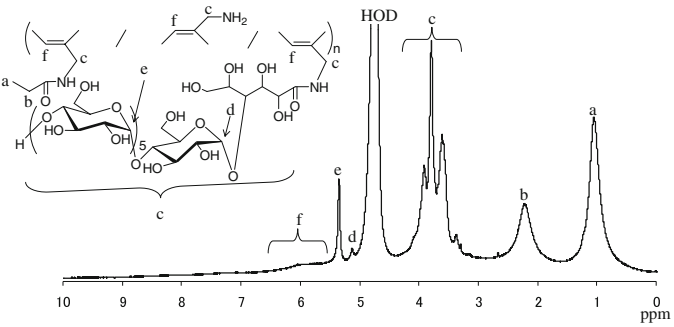


Fig. 3 ^{1}H NMR spectrum of **10** in D_2O

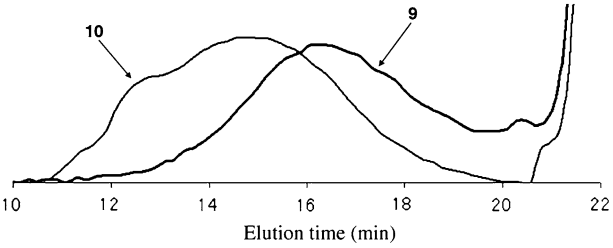


Fig. 4 GPC curves of **9** and **10** with 0.020 mol/L LiCl/DMF as the eluent

maltooligosaccharide-grafted polyacetylene **10**. The functionality of the maltooligosaccharide in **10** was calculated by the integrated ratio of the signal **a** to the signal **e** to be 5%, and accordingly the ratio among the units with pendant ethanamide, amine, and maltooligosaccharide was established based on the unit ratio of **9** to be 0.76:0.19:0.05. The GPC curve of the obtained **10** with 0.020 mol/L LiCl/DMF as the eluent was shifted to the region of the higher molecular weight compared with that of **9** as shown in Fig. 4, also supporting the progress of the functionalization by maltoheptaose lactone on **9**.

Enzymatic polymerization of **10** giving amylose-grafted polyacetylene

The phosphorylase-catalyzed enzymatic polymerization from **10** was performed using 50 equivalents of G-1-P for the primer chains in acetate buffer. The reaction solution was dialyzed to isolate the product, which was purified further by precipitation from methanol. The solubility of the product was same as that of a standard amylose, i.e., soluble in DMSO and alkaline aqueous solution. Figure 5 shows the ^{1}H NMR spectrum of the product in 1.0 mol/L NaOD/D_2O. The significant difference in the signal patterns of the spectra between before (Fig. 3) and after (Fig. 5) the polymerization was no appearance of the signals due to the main-chain protons and the H1 protons of the glucose residues closest to the main-chains. Furthermore, the relative intensities of the ethyl signals in Fig. 5 are lower than those in Fig. 3. These observations indicated the progress of the enzymatic

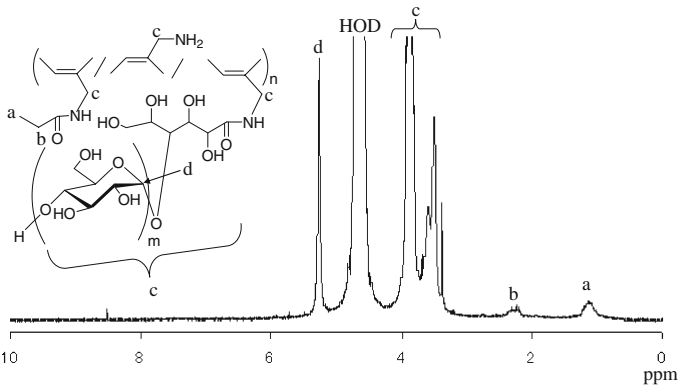


Fig. 5 ^{1}H NMR spectrum of **11** in 1.0 mol/L NaOD/D_2O

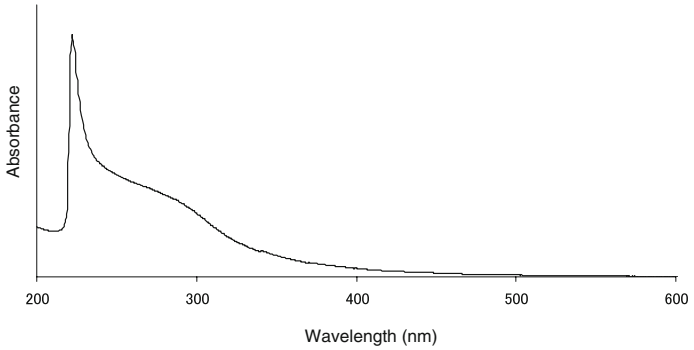
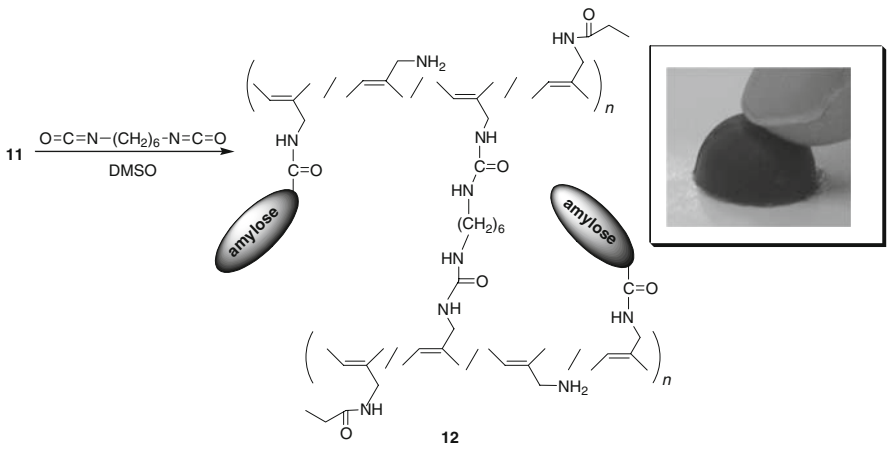


Fig. 6 UV–vis spectrum of **11** in 0.20 mol/L NaOH aqueous solution

polymerization, leading to the formation of saccharide chain (amylose) with the high DP depicted as the structure of **11** in Scheme 3. The UV–vis spectrum of **11** in 0.20 mol/L NaOH aqueous solution (Fig. 6) shows the wide absorptions at around 220–500 nm due to the conjugated main-chain of the polyacetylene accompanied with the overlapping absorption at 222 nm due to the amido groups. This data also supported that the product had the polyacetylene structure **11** carrying the amylose graft chains by the amido linkages.

Formation of organogel by cross-linking reaction of **11** with hexamethylene diisocyanate

According to the ratio of each unit in **10** as aforementioned, the amylose-grafted polyacetylene **11** certainly had the remaining free amino groups, which was used for the further reaction. To obtain the easily handled material from **11**, we attempted to form the gel by the cross-linking reaction of the amino groups in **11** with hexamethylene diisocyanate (Scheme 5). The reaction was carried out in DMSO at room temperature with stirring and subsequently kept at 80 °C to proceed the



Scheme 5 Cross-linking reaction of **11** with hexamethylene diisocyanate

gelation. The obtained gelic material was further treated with DMSO and kept under ambient conditions to give the organogel with DMSO as shown in Scheme 5. The IR spectrum of the obtained gel exhibited the carbonyl absorption ascribable to the urea linkage at 1624.0 cm^{-1}, which has not been appeared in the IR spectrum of **11**, accompanied with the carbonyl absorption of the amido linkage at 1647.1 cm^{-1}. This data indicated the reaction of the amine on **11** with the isocyanate group took place to produce the cross-linked material **12** with the urea linkages. When the cross-linking reaction of **9** or **10** with hexamethylene diisocyanate was carried out under the similar conditions as those described earlier, the insoluble solid materials were produced, but they were not gelic form with DMSO. This result suggested that the amylose graft chains on **11** strongly affect the stabilization of the gelic form with DMSO, probably caused by the provision for the space including DMSO molecules in the cross-linked material **12** due to the interaction among the long amylose chains. The content of DMSO in the gel was estimated by the weight difference in the dried material and the gel to be 67.3 wt.%. Figure 7 shows stress–strain curve under compression of the gel. The fracture stress and strain were 280 kPa and 88%,

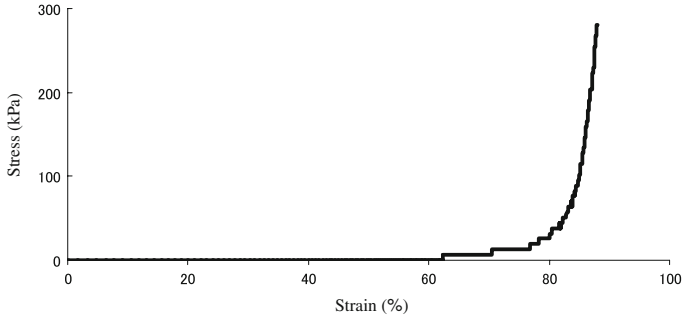


Fig. 7 Stress–strain curve under compression of the gel

respectively, indicating the high elastic nature of the gel. It can be considered that this easily handled gel has a possibility for the practical application as the new hybrid material of polyacetylene with amylose, which will be performed in our future study.

Conclusion

In this study, we attempted the chemoenzymatic synthesis of the amylose-grafted polyacetylene **11** with the high DP by the polymer reaction method. The polyacetylene **10** having the maltooligosaccharide chains was first synthesized by the reaction of amine-functionalized polyacetylene **9** with maltoheptaose lactone. Then, the phosphorylase-catalyzed enzymatic polymerization using G-1-P from the maltooligosaccharides on **10** was performed to give the polyacetylene **11** having amylose graft-chains. The structure of product was confirmed by the ^{1}H NMR and UV–vis spectra. Furthermore, **11** was converted into the organogel with DMSO by the cross-linking reaction of the amino groups existed on **11** with hexamethylene diisocyanate. The detailed evaluation of the gel as the new hybrid material of polyacetylene with amylose is now in progress in our research group.

Acknowledgments The authors are indebted to Ezaki Glico Co. Ltd, Osaka for the gift of phosphorylase. J. K. acknowledges the financial support from the Asahi Glass Foundation.

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