Triallyl Monomer Bearing Adamantane-like Core Derived from Naturally Occurring *myo*-Inositol: Synthesis and Polyaddition with Dithiols

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ABSTRACT: This paper deals with a triallyl monomer bearing a rigid adamantane-like core derived from *myo*-inositol, a naturally occurring cyclic hexaol. The core structure of the monomer can be readily constructed by orthoesterification of *myo*-inositol. The polyaddition of the triallyl monomer with dithiols based on the thermally induced radical thiol-ene reaction gives the corresponding networked polymers. These networked polymers exhibit much higher thermal stability than the comparative networked polymers obtained from a triallyl monomer bearing less rigid cyclohexyl core. © 2014 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 1193–1199

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INTRODUCTION Molecular design of multifunctional monomers for synthesis of networked polymers involves (1) design of their core structures, (2) choice of reactive functions to be attached on the cores, and (3) choice of the number of the reactive functions. By combining these factors appropriately, properties of the corresponding networked polymers can be adjusted specifically depending on various demands in practical applications. Particularly, rigidity of core structures of monomers, which will be introduced into the crosslinking points of the networked polymers, is a critical factor to determine the properties of the networked polymers. In general, the employment of monomers with rigid cores gives us an effective approach to obtain polymer materials with heat resistance and mechanical strength.[1–5]

Recently, our research interest has been focused on utilization of naturally occurring *myo*-inositol as a starting material for polymer synthesis,[6] with aiming that such investigation would contribute to the current progress in the development of bio-based polymers.[7–11] *myo*-Inositol is a cyclic hexaol that exists in organs as its phosphate derivatives such as phosphatidyl inositol and phytic acid.[12,13] A wide range of *myo*-inositol derivatives have been synthesized through various protocols of selective protection of hydroxyl groups.[14] Among those protocols, the orthoesterification of *myo*-inositol has been most frequently used for the selective and straightforward protection of the three hydroxyl groups at 1-, 3-, and 5-positions at once.[15] The resulting orthoesters are adamantane-like rigid compounds that are functionalized with three hydroxyl groups, of which selective chemical transformations give a wide range of *myo*-inositol-derivatives.[16–19] Upon looking at the adamantane-like molecular structure of *myo*-inositol 1,3,5-orthoesters, we envisaged its utilization as a precursor for synthesizing various trifunctional monomers with a rigid core. So far, only a few examples of polymers with *myo*-inositol 1,3,5-orthoester moieties have been reported:[20–22] In some of these examples, the orthoester pendants were hydrolyzed under acidic conditions to obtain cyclic polyol moieties, and their hydroxyl groups were phosphorylated to obtain polymer materials with metal ion-absorbing function.[20,21] On the other hand, Holmes et al. have reported efficient use of *myo*-inositol 1,3,5-orthoester as a rigid scaffold to design a *bis*(styryl)-type monomer.[22] The two styryl moieties of the monomer were oriented so that the monomer underwent the cyclopolymerization to give a linear polystyrene derivative. Finn et al. have reported a *tris*(propargylether) bearing *myo*-inositol 1,3,5-orthoester core.[23] With the azide-alkyne coupling chemistry, this monomer was converted into a networked polymer with high adhesion performance. However, the influence of the rigidity of the core on the properties of the networked polymers is not clarified therein.

The designed monomer for the present work is a *tris*(allylether)-type compound **2** that can be easily synthesized from *myo*-inositol 1,3,5-orthoacetaete **1**. The reasons for the choice of allyl group as the reactive site of the monomer are (1) its facile

Additional Supporting Information may be found in the online version of this article.

introduction under basic conditions that are compatible with the orthoester moiety and (2) its versatility that allows us to use it for various bond formation chemistries, such as hydrosilylation, metathesis, and thiol-ene chemistry. Currently, thiol-ene reaction, that is, radical addition of thiol to C—C double bond, is used as one of the "click" reactions for combining two components into one molecule quickly and quantitatively.[24,25] Its expanding application field includes polymers and polymeric biomaterials[26–28] and synthesis of functionalized monomers.[29–31] Recently, the exploitation of the thiol-ene reaction has opened a new access to networked polymers.[32–37]

Herein, we report the details of the synthesis of tris(allylether)-type monomer **2** and its radically mediated polyaddition with dithiols to afford networked polymers with rigid *myo*-inositol orthoester cores. Their thermal stability was compared with that of comparative networked polymers with less rigid cyclohexyl cores to clarify the influence of rigidity of cores on thermal stability.

EXPERIMENTAL

Chemicals

myo-Inositol (99.0%), allyl bromide (>99.0%), azobisisobutyronitrile (AIBN) (>98%), 1,6-hexanedithiol, 1,4-butanedithiol, *bis*(3-mercaptopropionyl)ethylene glycol were purchased from Wako Pure Chemical Industries Co., and used as received. *p*-Toluenesulfonic acid monohydrate (98.0%) and trimethyl orthoacetate (98.0%) were purchased from Tokyo Chemical Industry Co. and used as received. Triethylamine (99.0%) and 60% sodium hydride in mineral oil were purchased from Kishida Chemical Co. and used as received.

N,N-Dimethylformamide (DMF) (>95.5%) was purchased from Wako Pure Chemical Industries Co., dried over calcium hydride, and distilled under a reduced pressure prior to use. 1,4-Dioxane was purchased from Kishida Chemical Co. dried over calcium hydride, and distilled prior to use.

Instruments

NMR spectra (400 MHz for ^{1}H; 100.6 MHz for ^{13}C) were recorded on a JEOL-NMR spectrometer model JNM-AL400. Chemical shift δ and coupling constant J are given in ppm and Hz, respectively. IR spectra were obtained on a JASCO FT/IR-470 and wave number ν is given in cm^{-1}. Thermogravimetric analysis (TGA) was performed under a nitrogen flow in a range from 50 to 500 °C at a heating rate of 10 °C min^{-1} with a RIGAKU model Thermo plus EVO II TG-DTA. Differential scanning calorimetry (DSC) was performed under a nitrogen flow in a range from −100 to 50 °C at a heating rate of 10 °C min^{-1} with a SEIKO Instruments model EXSTAR6000. From the resulting DSC profiles, the glass transition temperatures (T_g) were obtained as the extrapolated onset temperatures.

Synthesis

Synthesis of myo-Inositol 1,3,5-Orthoacetate (1)

To a suspension of *myo*-inositol (12.0 g; 66.6 mmol) in DMF (100 mL), trimethyl orthoacetate (12.0 mL; 94.3 mmol) and *p*-toluenesulfonic acid monohydrate (1.0 g; 5.8 mmol) were added. The resulting mixture was heated at 100 °C for 2–3 h until the mixture became homogeneous. After cooling, triethylamine (4.0 mL) was added to the solution. The solution was evaporated to dryness under a reduced pressure, and the resulting residue was dissolved in a minimum amount of ethyl acetate and chromatographed on a short silica gel column with eluting with ethyl acetate. The resulting solution was concentrated under a reduced pressure, and the resulting residual solid was recrystallized from methanol to obtain *myo*-inositol 1,3,5-orthoacetate (**1**) (9.57 g; 46.3 mmol; 70%) as a colorless crystal.

Synthesis of 2,4,6-Tri-O-Allyl-myo-Inositol 1,3,5-Orthoacetate (2)

Sodium hydride in mineral oil (60%; 4.0 g; 0.10 mol) was washed with hexane (10 mL) twice, dried under vacuum, and then dispersed in DMF (20 mL). To the resulting dispersion, a solution of *myo*-inositol 1,3,5-orthoacetate (**1**) (4.15 g; 20.0 mmol) in DMF (30 mL) was added dropwise for 30 min at room temperature. After cooling to 0 °C, allyl bromide (6.1 mL; 70 mmol) was added to the mixture dropwise for 10 min. The resulting mixture was allowed to warm to room temperature and was stirred for 3 h. Water (15 mL) was added to the mixture carefully, and the resulting mixture was extracted with ethyl acetate (100 mL) three times. The combined organic layers were dried over sodium sulfate, filtered, and concentrated under a reduced pressure. The resulting residue was distilled under vacuum to obtain 2,4,6-tri-*O*-allyl-*myo*-inositol 1,3,5-orthoacetate (**2**) (5.27 g; 16.2 mmol; 81%) as a colorless oil: ^{1}H-NMR (in $CDCl_3$, at rt) 6.04–5.93 (m, 1H), 5.92–5.83 (m, 2H), 5.35–5.26 (m, 3H), 5.23–5.17 (m, 3H), 4.35–3.30 (m, 3H), 3.23 (t, $J = 3.7$, 2H), 4.18 (d, $J = 5.6$, 2H), 4.13–4.01 (m, 4H), 3.85 (t, $J = 1.6$, 1H), 1.46 (s, 3H); ^{13}C-NMR (in $CDCl_3$, at rt) 134.71, 134.13, 117.49, 117.24, 108.92, 73.58, 71.25, 70.55, 70.47, 68.06, 66.32, 24.27; IR (on a NaCl plate) 3080, 3012, 2955, 2865, 1645 cm^{-1}. Anal. calcd. for $C_{17}H_{24}O_6$: C 62.94, H 7.46, N 0.00; found: C 62.60, H 7.56, N 0.00.

Synthesis of 2,4,6-Tri-O-Allyl-myo-Inositol (3)

To a solution of **2** (1.62 g; 5.00 mmol) in ethanol (10 mL), 1M HCl aq (10 mL) was added, and the resulting mixture was heated with refluxing. After 24, the mixture was concentrated under a reduced pressure, and the resulting residue was chromatographed on a silica gel column [eluent = hexane + ethyl acetate (1:1)] to obtain 2,4,6-tri-*O*-allyl-*myo*-inositol (**3**) (1.45 g; 4.83 mmol; 97%) as a white solid: ^{1}H-NMR (in $CDCl_3$, at rt) 6.04–5.88 (m, 3H), 5.35-5.24 (m, 3H), 5.23-5.26 (m, 3H), 4.42-4.29 (m, 6H), 3.91 (s, 1H), 3.60-3.35 (m, 5H), 2.62 (s, 1H), 2.46 (d, $J = 2.3$, 2H); ^{13}C-NMR (in $CDCl_3$ at rt) 134.99, 134.89, 117.23, 116.90, 81.63, 79.09, 74.68, 74.23, 73.90, 72.30; IR (KBr) 3414, 3076, 2922, 1132, 714 cm^{-1}.

Synthesis of 1,3,5-Tri-O-Methyl-2,4,6-Tri-O-Allyl-myo-Inositol (4)

Sodium hydride in mineral oil (60%; 0.82 g; 20 mmol) was washed with hexane (5 mL) twice, dried under vacuum, and

then dispersed in DMF (10 mL). To the resulting dispersion, a solution of **3** (1.20 g; 4.00 mmol) in DMF (24 mL) was added dropwise for 10 min at room temperature. After cooling to 0 °C, dimethyl sulfate (2.3 g; 18 mmol) was added to the mixture dropwise for 10 min. The resulting mixture was allowed to warm to room temperature and was stirred for 24 h. Water (6 mL) was added to the mixture carefully, and the resulting mixture was extracted with ethyl acetate (30 mL) three times. The combined organic layers were dried over sodium sulfate, filtered, and concentrated under a reduced pressure. The resulting residual oil was chromatographed on a silica gel column (eluent = hexane + ethyl acetate (5:1)) to obtain 1,3,5-tri-*O*-methyl-2,4,6-tri-*O*-allyl-*myo*-inositol (**4**) (1.14 g; 3.34 mmol; 84%) as a colorless oil: ^{1}H-NMR (in $CDCl_3$ at rt) 6.05–5.85 (m, 3H), 5.33–5.22 (m, 3H), 5.28–5.23 (m,3H), 4.35–4.21 (m, 6H), 4.00 (t, $J = 2.$ 4, 1H), 3.63 (t, $J = 9.5$, 2H), 3.62 (s, 3H), 3.46 (s, 6H), 3.02 (t, $J = 9.2$, 1H), 2.99,2.96 (dd, $J = 2.2$, 2.4, 2H); ^{13}C-NMR (in $CDCl_3$, at rt) 135.55, 116.48, 116.30, 85.43, 82.57, 81.27, 74.24, 73.00, 72.34, 61.27, 58.49; IR (on a NaCl plate) 3078, 2980, 2930, 1728, 1131, 721 cm^{-1}. Anal. calcd. for $C_{18}H_{30}O_6$: C 63.14, H 8.83, N 0.00; found: C 62.93, H 8.80, N 0.00.

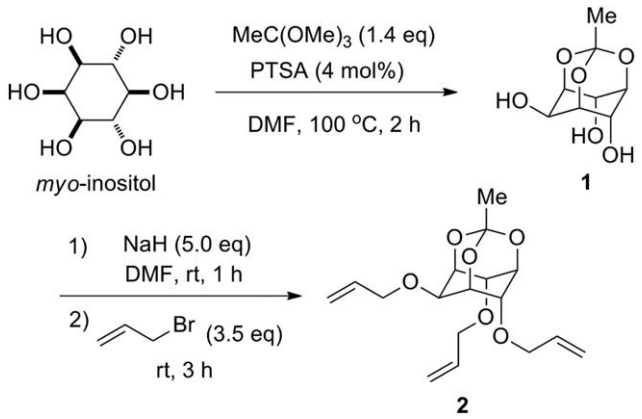
Radical Addition of 1-Octanethiol to Triallyl Monomer 2

Triallyl monomer **2** (496 mg; 1.53 mmol), AIBN (23 mg, 0.14 mmol) and 1-octanethiol (746 mg, 5.10 mmol) were placed in a vessel. To the mixture, 1,4-dioxane (3.1 mL) was added, and the reaction vessel was flushed with argon. The resulting solution was stirred at 65 °C for 4 h. The volatiles were removed under a reduced pressure, and the resulting residue was chromatographed on a silica gel column (eluent: hexane + ethyl acetate 20:1 + 2% triethylamine) to obtain a mixture of target **5** and its isomers (1.09 g; 1.43 mmol; 93%) as a slightly yellow oil: ^{1}H-NMR (in $CDCl_3$ at, rt) 4.32 (d, $J = 3.2$, 3H), 4.16 (t, $J = 3.7$, 2H), 3.70 (t, $J = 6.3$, 3H), 3.66–3.54 (m, 4H), 2.64 (t, $J = 7.2$, 2H), 2.57 (t, $J = 7.1$, 4H), 2.53–2.44 (m, 6H), 1.98–1.91 (m, 4H), 1.91–1.70 (m, 4H), 1.66–1.50 (m, 6H), 1.43–1.31 (m, 6H), 1.31–1.18 (m, 24H), 0.88 (t, $J = 6.8$, 9H); ^{13}C-NMR (in $CDCl_3$, at rt) 108.82, 74.31, 70.78, 68.13, 67.78, 67.63, 66.93, 31.93, 31.66, 29.60, 29.53, 29.49, 29.05, 28.80, 28.47, 28.37, 24.23, 22.48, 13.93; IR (on a NaCl plate) 2924, 2854, 1302, 1117, 867 cm^{-1}.

Polyaddition of Triallyl Monomer 2 and Dithiols

Typical procedure: Triallyl monomer **2** (497 mg; 1.50 mmol), AIBN (23 mg, 0.14 mmol), and 1,6-hexanedithiol (346 mg; 2.30 mmol) were placed in a vessel. To the mixture, 1,4-dioxane (3.1 mL) was added, and the reaction vessel was flushed with argon. The resulting solution was stirred at 65 °C for 4 h to obtain a transparent gel. After adding triethylamine (1 mL), the gel was crushed into pieces and washed with diethyl ether (10 mL). The resulting rubbery solid was isolated by filtration with suction and dried under vacuum at 60 °C for 24 h to obtain networked polymer **6b** (0.787 g; 96%): IR 2923, 2854, 1301, 1109, 865 cm^{-1}.

According to the typical procedure, the reaction of triallyl monomer **2** (497 mg; 1.50 mmol) and 1,4-butanedithiol (282 mg; 2.31 mmol) was carried out to obtain networked polymer **6a** (652 mg; 76%): IR 2932, 2850, 1302, 1106, 863 cm^{-1}.



SCHEME 1 Synthesis of triallyl monomer **2**.

According to the typical procedure, the reaction of triallyl monomer **2** (497 mg; 1.50 mmol) and *bis*(3-mercaptopropionic acid) ethylene glycol (551 mg; 2.31 mmol) was performed to obtain the corresponding networked polymer **6c** (990 mg; 94%): IR 2950, 2873, 1735, 1112, 1280, 867 cm^{-1}.

Polyaddition of Triallyl Monomer 4 and Dithiols

Typical procedure: Triallyl monomer **4** (514 mg; 1.50 mmol), AIBN (0.338 g; 2.25 mmol), and 1,6-hexanedithiol (338 mg; 2.25 mmol) were placed in a vessel. To the mixture, 1,4-dioxane (3.1 mL) was added, and the reaction vessel was flushed with argon. The resulting solution was stirred at 65 °C for 4 h to obtain a transparent gel. The gel was crushed into pieces and washed with diethyl ether (10 mL). The resulting rubbery solid was isolated by filtration with suction and dried under vacuum at 60 °C for 24 h to obtain networked polymer **7b** (836 mg; 98%): IR 2918, 2850, 1129, 1094, 703 cm^{-1}.

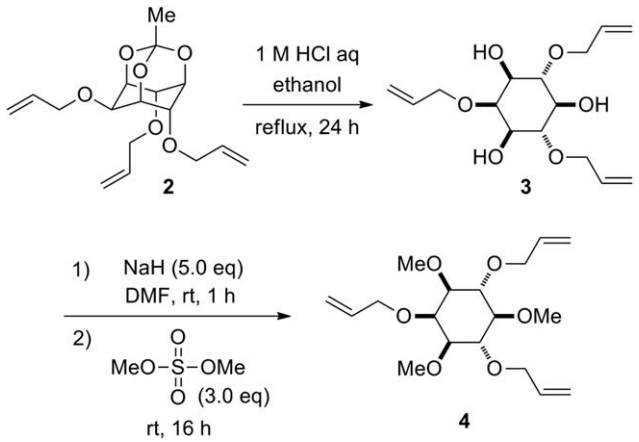
According to the typical procedure, the reaction of triallyl monomer **4** (527 mg; 1.54 mmol) and 1,4-butanedithiol (282 mg; 2.31 mmol) was carried out to obtain networked polymer **7a** (598 mg; 74%): IR 2926, 2807, 1130, 1095, 711 cm^{-1}.

According to the typical procedure, the reaction of triallyl monomer **4** (527 mg; 1.54 mmol) and *bis*(3-mercaptopropionic acid) ethylene glycol (551 mg; 2.31 mmol) was performed to obtain the corresponding networked polymer **7c** (1.00 g; 93%): IR 2931, 1738, 1131, 1095, 711 cm^{-1}.

RESULTS AND DISCUSSION

Synthesis of Triallyl Monomer

Scheme 1 shows the synthetic route to the triallyl monomer **2**. Treatment of *myo*-inositol with trimethyl orthoacetate in the presence of a catalytic amount of *p*-toluenesulfonic acid resulted in the selective orthoesterification of *myo*-inositol. The resulting triol **1** with a rigid core was isolated in 70%



SCHEME 2 Synthesis of triallyl monomer **4**.

by recrystallization from methanol. The next reaction step, allylation of the hydroxyl groups of **1**, was achieved by a standard protocol, that is, transformation of hydroxyl group into sodium alkoxide with sodium hydride and successive treatment with allyl bromide. The reaction proceeded quantitatively and the resulting **2** was isolated in a pure form by distillation under vacuum. Its structure was confirmed by ^{1}H and ^{13}C-NMR spectroscopies (Fig. S1 in Supporting Information): The ^{1}H-NMR spectrum indicated a singlet signal attributable to the methyl group at 1.46 ppm and signals for the vinyl protons in a range from 5 to 6 ppm. The integration ratio between these signals agreed with the monomer structure bearing one orthoester core and three allyl moieties. The ^{13}C-NMR spectrum indicated a signal at 109 ppm attributable to the carbon connecting to the three oxygen atoms in the orthoester structure. In addition, the signal assignments were supported by C-H COSY spectroscopy (Fig. S2 in Supporting Information).

Synthesis of a Comparative Triallyl Monomer with a Less Rigid Structure

Besides the triallyl monomer **1** with a rigid orthoester core, another triallyl monomer **4** with a less rigid structure was prepared (Sch. 2). The starting material used herein was the triallyl monomer **2**. Its orthoester core was hydrolyzed under acidic conditions to obtain triol **3**. The three hydroxyl groups of **3** were transformed into the corresponding methyl ether using sodium hydride and dimethyl sulfate to obtain **4**. The triallyl monomer **4** was isolated successfully by column chromatography. Its structure was confirmed by ^{1}H and ^{13}C-NMR spectroscopy (Fig. S3 in Supporting Information).

Model Reaction

Next, we investigated radical addition of monofunctional thiol to the allyl groups of **2** to clarify the efficiency of the reaction and the stability of the orthoester moiety under the conditions (Sch. 3).

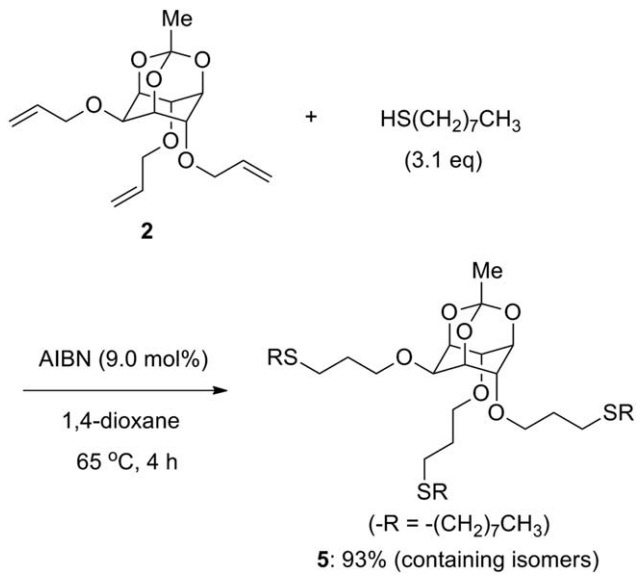
With employing AIBN as a radical source, the reaction of **2** and 1-octanethiol was carried out in 1,4-dioxane at 65 °C. Monitoring the reaction with thin layer chromatography revealed complete consumption of **2** within 4 h and formation of the corresponding adduct **5**. Besides the formation of **5**, those of minor products were detected. These products were quite similar to **5** in terms of polarity and thus were considered to be regioisomers that were formed as a result of the incomplete control in regioselectivity in the radical addition of thiol to C—C double bond. Since it was difficult to separate them by column chromatography, **5** and its isomers were collected in one fraction and the mixture was analyzed by NMR spectroscopy. The resulting ^{1}H-NMR spectrum is shown in Figure 1.

Besides the set of major signals attributable to **5**, the spectrum also showed some small signals attributable to the isomers formed by the addition of thiol to the center carbon of the allyl group.[38,39] A list of the possible regioisomers is shown in Figure S4 in Supporting Information. The ^{13}C-NMR spectrum, which also supported the structure of **5**, is shown in Figure S5 in Supporting Information. In addition, the signal assignments were supported by C—H COSY spectroscopy (Fig. S6 in Supporting Information).

Synthesis of Networked Polymers

Scheme 4 shows the reaction of triallyl monomers **2** and **4** with dithiols to synthesize networked polymers. Table 1 summarizes the results. The conditions for the reaction were same as those for the model reactions with using monothiols.

The reactions of **2** with 1,4-butanedithiol (BDT), 1,6-hexanedithiol (HDT), and *bis*(3-mercaptopropionic acid) ethylene glycol (BMPEG) gave the corresponding networked polymers **6a**, **6b**, and **6c**, respectively. In a similar manner, the reactions of triallyl monomer **4** with the dithiols were performed to obtain a series of the corresponding networked polymers **7**. In all the cases, the reaction gave a transparent gel. From



SCHEME 3 Radical addition reaction of monothiols to the allyl moieties of triallyl monomer **2**.

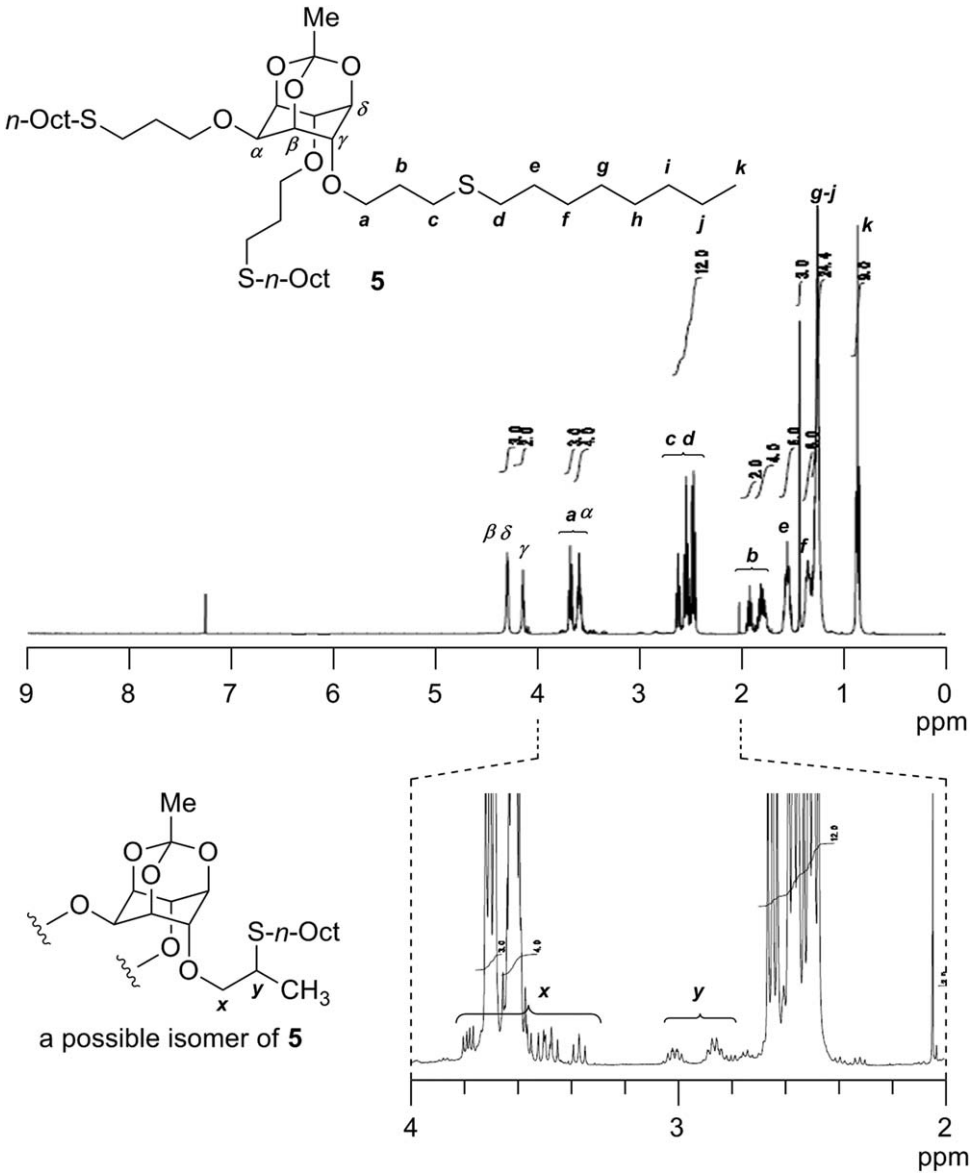


FIGURE 1 ^{1}H-NMR spectrum of compound **5**.

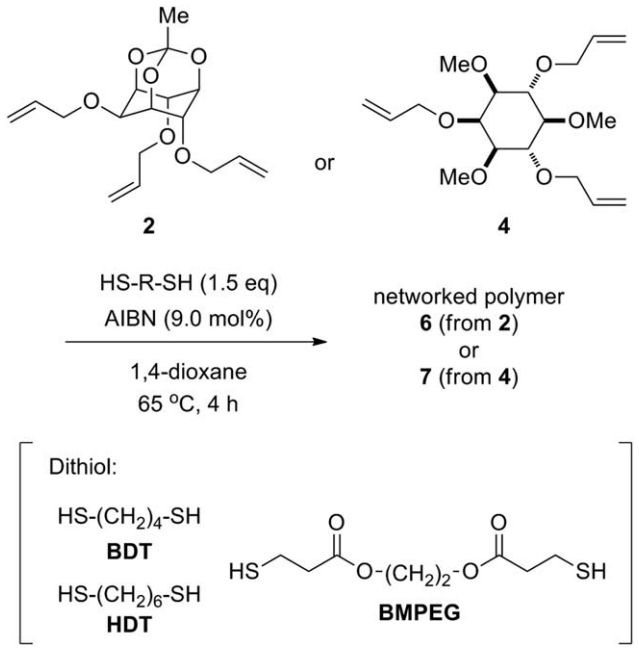
this gel, the networked polymers were isolated as diethyl ether-insoluble fractions.

As shown in Table 1, the yields of the networked polymers that were isolated as ether-insoluble fractions were excellent when the triallyl monomers were reacted with HDT and BMPEG (entries 2 and 3, entries 5 and 6). In contrast, the yields of **6a** and **7a** that were synthesized using BDT were moderate (entries 1 and 4), to imply that the chain length of BDT was less suitable for efficient intermolecular polyaddition (Fig. S7 in Supporting Information). As a result, intramolecular addition was enhanced to give increased amount of macrocyclic structures, leading to the decrease in crosslinking density.

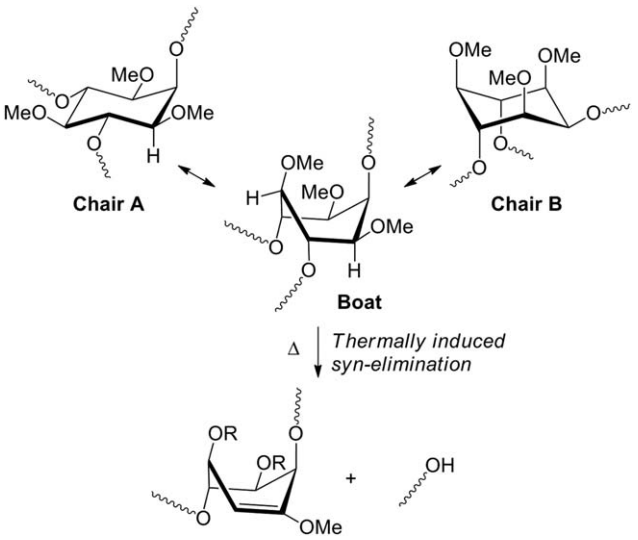
Thermal Properties of the Networked Polymers

The obtained networked polymers were subjected to TGA. The resulting TGA traces are shown in Figure S8 in Supporting Information. From the corresponding thermal profiles, 5% weight loss temperature (T_{d5}) and 10% weight loss temperature (T_{d10}) were extracted (Table 1). The T_{d5} and T_{d10} values for the networked polymers **6** were higher than 300 and 330 °C, respectively. In contrast to these values, those for the networked polymers **7** were much lower, to clarify the higher thermal stability of **6** than **7**.

The difference in thermal stability between **6** and **7** can be attributable to the difference in conformational freedom between the two different inositol-derived cores. As shown in Scheme 5, the inositol-derived six-membered ring in the networked polymers **7** is allowed to have two chair-like conformations (Chairs A and B), and these two chairs are intermediated by boat-like conformations. One of the boat-like conformations depicted in Scheme 5 is favorable for thermally induced *syn*-elimination to give fragmented polymers



SCHEME 4 Synthesis of networked polymers.



SCHEME 5 Possible mechanism for the thermal degradation of networked polymer **7**.

with hydroxyl terminal. Further conformational change of the six-membered ring allows stepwise elimination of alcohols that causes thermal degradation of the networked polymers. On the other hand, the orthoester-type core of **6** is highly rigid to prohibit its conformational change into boat-like one. This efficient "conformation freeze" contributed to the enhanced thermal stability of the networked polymers **6**.

Among the networked polymers **6**, **6b** obtained using HMDT as dithiol monomer was thermally most stable. It was much more stable than **6a** obtained by using another alkyl dithiol, BDT. This difference in thermal stability between these networked polymers is attributable to the difference in crosslinking density. As has been already discussed above, the intermolecular reaction between triallyl monomer **2** and dithiols leading to the formation of crosslinking points is competed by the intramolecular reaction that terminate the growth of networked structure. The much higher yield of **6b** that was obtained as ether-insoluble fraction than that of **6a** obtained in a similar way implies the higher efficiency in growth of networked structure in **6b** than that in **6a**, and this tendency is in a good agreement with the much higher thermal stability of **6b** than **6a**. On the other hand, the networked polymer **6c** obtained using BMPEG was thermally less stable than **6b**, although the high yield of **6c** suggests efficient growth of the networked structure. The lower stability of **6c** would be due to the longer chain length of the BMPEG-derived tether between the two sulfur atoms and presence of the ester linkage in the tether that can be thermally less stable than the other linkages such as ether and thioether ones. These discussions on the order of thermal stability, **6b** > **6c** > **6a**, can be adopted also to that of the thermal stability of the networked polymers **7**, **7b** > **7c** > **7a**.

For further clarification of the influence of rigidity of core structure on the properties of the networked polymers, the networked polymers **6** and **7** were subjected to DSC analysis. The resulting DSC profiles are shown in Figure S9 (Supporting Information). From these profiles, the T_g values were obtained and listed in Table 1. As was expected from the rubbery nature of the networked polymers, all the T_g values

TABLE 1 Synthesis of Networked Polymers and their Thermal Stability.

Entry	Triallyl monomer	Dithiol	Networked polymer	Yield (%)[a]	T_{d5} (°C)[b]	T_{d10} (°C)[b]	T_g (°C)[c]
1	**2**	**BDT**	**6a**	76	302	330	1
2	**2**	**HDT**	**6b**	93	327	339	1
3	**2**	**BMPEG**	**6c**	94	310	334	−10
4	**4**	**BDT**	**7a**	74	269	293	−10
5	**4**	**HDT**	**7b**	98	307	329	−6
6	**4**	**BMPEG**	**7c**	93	295	309	−27

[a] Ether-insoluble parts.
[b] Determined by TGA.
[c] Determined by DSC.

were lower than ambient temperature. The T_g values of the networked polymers **6** bearing the adamantane-like structure at the crosslinking points were higher than those of the networked polymers **7** bearing the cyclohexyl structure at the crosslinking points, implying that the difference in the T_g values between **6** and **7** can be correlated with the difference in the rigidity between the adamantane-like structure and the cyclohexyl one: the much less freedom in the conformational change of the adamantane-like core than that in the conformational change of the cyclohexyl core would be responsible for the higher T_g values of **6** than that of **7**.

CONCLUSIONS

A naturally occurring *myo*-inositol was transformed into a triallyl compound with a rigid adamantane-like core via a sequence of two reaction steps: (1) 1,3,5-orthoesterification into the corresponding 2,4,6-triol and (2) allylation of the triol under basic conditions. The triallyl compound thus prepared was coupled with dithiols based on the radically mediated thiol-ene reaction. The consequent polyaddition that proceeded smoothly at 65 °C gave the corresponding networked polymers almost quantitatively. The resulting networked polymers with the adamantane-like structure at the crosslinking points were more heat-resistant than those obtained by an analogous polyaddition system with using a comparative triallyl monomer bearing a less rigid cyclohexyl core, to imply that the restriction of conformational change in the constrained adamantane-like structure hampered its thermally induced destruction.

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