Novel synthetic route of a trehalose-based linear polymer by ring opening of two epoxy groups with aliphatic diamine

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Abstract

A diepoxide compound derived from trehalose, 2,3-anhyrdo-4,6-*O*-benzylidene-α-D-allopyranosyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside, was synthesized and reacted with aliphatic diamines. The ring-opening reaction was carried out in 1-methyl-2-pyrrolidone (NMP) in the presence of triphenylphosphine (TPP), tris(4-methoxyphenyl)phosphine (TMPP) or 2-ehtyl-4-methylimidazole (2E4MIm), as a base catalyst. The reaction of the diepoxide compound with 1,6-diaminohexane yielded a soluble polymer with weight average molecular weight $(M_w) \sim 6300$ (GPC) and did not yield insoluble matter. The reaction of the diepoxide compound with N,N'-dimethyl-1,6-diaminohexane yielded a polymer with $M_w \sim 6500$ (GPC). The product was soluble in many organic solvents such as NMP, N,N-dimethylformamide (DMF), tetrahydrofuran (THF), acetone, toluene and ethyl acetate. Thermal analysis with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) revealed that the glass transition temperature of the polymer was $\sim 100\,^\circ$C and that the degradation temperature was $\sim 320\,^\circ$C.

1. Introduction

Utilization of renewable resources in polymer preparation is becoming more and more important. Many researches have been devoted to plasticization of polysaccharides (Fringant, Desbrières, & Rinaudo, 1996; Isogai, Ishizu, & Nakano, 1985; Lee & Shiraishi, 2001; Shibata, Asahina, Teramoto, & Yosomiya, 2001; Wolff, Olds, & Hilbert, 1951). However, the backbone of the polymer could not be changed freely when polysaccharides were chosen as starting materials. For the purpose to increase variation of polymer backbones, mono- or disaccharides are preferred as a monomer unit. Some researchers proposed the strategy for incorporation of mono- or disaccharide units into a polymer chain to yield polyurethane (Garçon et al., 2001; Hashimoto, Wibullcksanakul, & Okada, 1995), polyurea (Kurita et al., 1994), polyacetal (Maslinska-Solich, 2001; Teramoto,

Shibasaki, Arai, & Shibata, 2004), polyester (Okada, Tachikawa, & Aoi, 1997; Park, Kim, & Dordick, 2000; Uyama, Klegraf, Wada, & Kobayashi, 2000), and so on.

Cycloaliphatic epoxy resins has attracted attentions for their unique properties in recent years (Hartwig & Sebald, 2003; Soucek, Abu-Shanab, Anderson, & Wu, 1998; Tokizawa, Okada, Wakabayashi, Kimura, & Fukutani, 1993; Xie & Wang, 2001). We proposed herein a cycloaliphatic epoxide derived from a saccharide as a novel epoxy monomer. Saccharide-based epoxides have been researched for a long time (Baer & Radatus, 1984; Feast, Overend, & Williams, 1965; Hanessian & Plessas, 1969; Horton & Hutson, 1966; Hough, Munroe, & Richardson, 1971). However, in most of these researches, the saccharide-based epoxide was merely an intermediate to synthesis of amino-sugars, deoxy-sugars, antibiotics and so on. Baer and Radatus (1984) and Hough et al. (1971) synthesized 2,3:2′,3′-diepoxides from the 4,6:4′,6′-dibenzylidene acetal of α,α-trehalose. Trehalose is a symmetric α-(1–1′) linked non-reducing disaccharide, and very attractive resources as a monomer (Kurita et al., 1994; Park et al., 2000;

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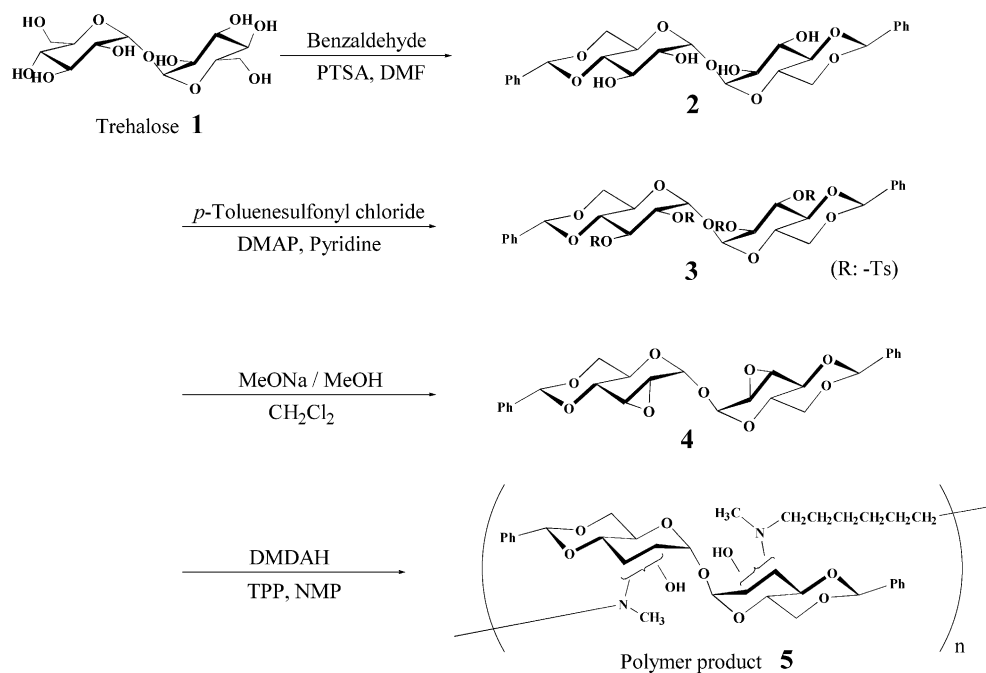
Scheme 1. Synthesis of a trehalose-based diepoxide compound **4** and a linear polymer **5**.

Teramoto et al., 2004), because of the chemical stability and the symmetrical structure. Recently, Hayashibara Co. Ltd developed an inexpensive and environment-friendly manufacturing process of α,α-D-trehalose (**1**) by the enzymatic conversion of starch (Kubota, Sugimoto, & Miyake, 1999). In the present study, we synthesized a trehalose-based diepoxide compound, 2,3-anhyrdo-4,6-*O*-benzylidene-α-D-allopyranosyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside (**4**), following the literatures (Baer & Radatus, 1984) with some modification, and investigated its reactivity with aliphatic diamines (Scheme 1). We intend to apply the diepoxy compound as a novel epoxy monomer for linear and cross-linked polymers.

2. Experimental

2.1. Materials

α,α-D-Trehalose dihydrate kindly provided by Hayashibara Co., Ltd (Japan) was dehydrated at 130 °C for 24 h before use. *N,N*-Dimethylformamide (DMF; anhydrous), 1-methyl-2-pyrrolidinone (NMP; anhydrous), and tris(4-methoxyphenyl)phosphine (TMPP) were used as received from Aldrich Chemical Company. Other organic solvents, sodium methoxide, and *p*-toluenesulfonyl chloride were purchased from Kanto Kagaku (Japan). Benzaldehyde, *p*-toluenesulfonic acid, triphenylphosphine (TPP) were purchased from Kishida Chemical (Japan). 4-Dimethylaminopyridine (DMAP), 2-ehtyl-4-methylimidazole (2E4MIm), 1,6-diaminohexane (DAH) and *N,N′*-dimethyl-1,6-diamino

hexane (DMDAH) were purchased from Tokyo Kasei Kogyo (Japan). These reagents were used as received.

2.2. Synthesis of 4,6-O-benzylidene-α-D-glucopyranosyl 4,6-O-benzylidene-α-D-glucopyranoside (2)

Benzaldehyde (146 ml, 1.43 mol) was mixed with *p*-toluenesulfonic acid (PTSA, 10.9 g, 0.057 mol) and sodium sulfate anhydrous (37 g) in 580 ml of anhydrous methanol, and the mixture was refluxed under a nitrogen atmosphere for 24 h. After filtration to remove sodium sulfate, the filtrate was concentrated by a rotary evaporator to give an yellow sticky liquid. To this liquid was added 715 ml of DMF and dried trehalose **1** (73.43 g, 0.22 mol), and reaction was carried out at 40–50 °C under 300 Torr for 24 h. After concentration by the rotary evaporator, the product was suspended in diethylether, and neutralized by washing the organic phase several times with sodium hydrogen carbonate aqueous solution. Chloroform was added to the organic phase, and the precipitate was gathered on a filter paper. The precipitate was washed with deionized water and dried in vacuo for 1 day to give a white powder of 4,6:4′,6′-di-*O*-benzylidene-α,α-D-trehalose **2** (90.6 g, 81% yield). IR (KBr): 3500 (OH), 3100 (aromatic CH), 2950, 2900 (aliphatic CH), 1450 (aromatic C=C), 1080, 990 (acetal), 750, 700 cm^{-1} (aromatic C–H); ^{1}H NMR (DMSO-d_6, 400 MHz,) $\delta = 7.49$ (d, 4H, aromatic), 7.41 (d, 6H, aromatic), 5.61 (s, 2H, >C*H*Ph), 5.36 (d, 2H, O*H*), 5.29 (d, 2H, O*H*), 4.99 (d, 2H, *H-1*), 4.2–4.0 (m, 4H, *H-4,6*), 3.8 (m, 2H, *H-5*), 3.7 (t, 2H, *H-3*), 3.4 (overlapping with resonance of water, 2H, *H-2*).

2.3. Synthesis of 4,6-O-benzylidene-2,3-di-O-tolylsulfonyl-α-D-glucopyranosyl 4,6-O-benzylidene-2,3-di-O-tolylsulfonyl-α-D-glucopyranoside (3)

To a solution of di-O-benzylidenetrehalose **2** (89.3 g, 0.17 mol) in 510 ml of pyridine was added 4-dimethylaminopyridine (DMAP, 2.2 g, 0.018 mol) and *p*-toluenesulfonyl chloride (193.7 g, 1.02 mol), and the solution was stirred at 80 °C under a nitrogen atmosphere for 24 h. After subsequent addition of *p*-toluenesulfonyl chloride (48.2 g, 0.25 mol), stirring was continued for 24 h under the same condition to complete the tosylation. The dark-brown solution was concentrated to a small volume by the rotary evaporator, and poured into excess water to give a brown precipitate. The product was washed each three times with water and ethanol, and redissolved in 1.3 l of chloroform. After passage through celite, the resulting orange solution was evaporated to less than half volume and poured into 400 ml of hot ethanol. After cooling to room temperature, the precipitate was gathered on a filter paper and dried in vacuo for 1 day to give a pale brown powder of 4,6:4′,6′-di-O-benzylidene-tetra-O-tosyl-α,α-D-trehalose **3** (137.2 g, 70% yield). IR (KBr): 3100 (aromatic CH), 2950, 2900 (aliphatic CH), 1600, 1500, 1450 (aromatic C=C), 1370, 1180 (S=O), 1040, 990 (acetal), 980, 830 (S–O–C), 750, 700 cm^{-1} (aromatic C–H); ^{1}H NMR (DMSO-d_6, 400 MHz), $\delta = 7.84$, 7.55, 7.4–7.0, 6.79 (26H, aromatic), 5.60 (s, 2H, >C*H*Ph), 5.22 (s, 2H, O*H*), 5.02 (t, 2H, *H-3*), 4.68 (q, 2H, *H-2*), 4.46 (q, 2H, *H-4*), 4.12 (m, 2H, *H-5*), 3.54 (m, 4H, *H-6*), 2.33 (s, 6H, PhC*H₃*), 2.14 (s, 6H, PhC*H₃*).

2.4. Synthesis of 2,3-anhydro-4,6-O-benzylidene-α-D-glucopyranosyl 2,3-anhydro-4,6-O-benzylidene-α-D-glucopyranoside (4)

Sodium methoxide (15.2 g) dissolved in 130 ml of methanol was added dropwise to the solution of di-O-benzylidene-tetra-O-tosyltrehalose **3** (40.0 g, 0.035 mol) in 420 ml of dichrolomethane. A precipitate was yielded after stirring at room temperature under nitrogen atmosphere for 3 days. The precipitate was separated from the filtrate by centrifugation and gathering on a filter paper, and washed with dichloromethane, water, ethanol, and acetone, followed by drying at room temperature in vacuo for 1 day (the first crop). The dichloromethane washings were concentrated by a rotary evaporator, combined with the filtrate, and stirred at room temperature for another 3 days. This procedure yielded a precipitate, and it was separated from the filtrate by centrifugation and gathering on a filter paper. After washing with dichloromethane, water, ethanol, and acetone, the product was dried at room temperature in vacuo for 1 day (the second crop). These crops were combined, recrystallized from hot DMF, and dried in vacuo for several days to give a white crystalline of 2,3:2′,3′-dianhydro-4,6:4′,6′-di-O-benzylidene-α,α-D-trehalose **4** (9.7 g, 57% yield). IR (KBr): 3100 (aromatic CH), 3000, 2950, 2900 (aliphatic CH), 1450 (aromatic C=C), 1250 (epoxy), 1050, 1010 (acetal), 900 (epoxy), 750, 700 cm^{-1} (aromatic C–H); ^{1}H NMR (DMF-d_7, 400 MHz), $\delta = 7.48$ (q, 4H, aromatic), 7.36 (m, 6H, aromatic), 5.71 (s, 2H, >C*H*Ph), 5.43 (d, 2H, *H-1*), 4.23–4.18 (q, 2H, *H-6a*), 4.13–4.02 (m, 4H, *H-4, H-5*), 3.73 (t, 2H, *H-6b*), 3.64 (q, 2H, *H-2*), 3.58 (d, 2H, *H-3*); $C_{26}H_{26}O_9$ (482.47): Calcd. C 64.72, H 5.43, Found C 64.63, H 5.44.

2.5. Polymerization of diepoxide 4 with aliphatic diamine

The diepoxide **4** and diamine were mixed in NMP in a molar ratio 1:1. TPP, TMPP or 2E4MIm was added to the mixture as a basic catalyst in 5 or 10 wt% to the total monomer weight. The mixture was heated under nitrogen atmosphere. The diepoxide **4** was not dissolved in the solvent until the mixture was heated to 90 °C. After the reaction, the solution was concentrated by the rotary evaporator and poured into excess water to yield a white precipitate. The precipitate was washed with water to remove unreacted diamine and dried at room temperature in vacuo for 1 day. The residue was redissolved in chloroform, and insoluble matter which mainly contains the unreacted diepoxide **4** was removed. The filtrate was concentrated by the rotary evaporator, followed by drying at room temperature in vacuo for 1 day. IR (KBr) (**4** reacted with DMDAH): 3500 (OH), 3100 (aromatic CH), 2950, 2900 (aliphatic CH), 1450 (aromatic C=C), 1050, 1010 (acetal), 750, 700 cm^{-1} (aromatic C–H); ^{1}H NMR (**4** reacted with DMDAH, CDCl₃-d_7, 400 MHz), $\delta = 7.50$ (m, 4H, aromatic), 7.36 (s, 6H, aromatic), 5.7–5.4 (m, 2H, >C*H*Ph), 5.4–5.2 (m, 2H, *H-1*), 4.4–3.5 (m, 12H, >C*H*-2-O-, >*CH*-3-O-, *H-4, H-5, H-6, OH*), 3.5–3.0 (m, 2H, >C*H*-2-N<, >C*H*-3-N<), 3.0–2.3 (m, 10H, –C*H₂*-N<, C*H₃*-N<), 1.6–1.4 (s, 4H, –C*H₂*–), 1.4–1.2 (s, 4H, –C*H₂*–).

2.6. Characterization

Fourier transform infrared (FT-IR) spectra were recorded on a Shimadzu FT-IR 8100 by the KBr-pellet method. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker AMX-400 (400 MHz) using DMSO-d_6, DMF-d_7, or CDCl₃ as a solvent. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) was performed at the linear mode on a Shimadzu/Kratos Kompact Probe, using α-cyano-4-hydroxycinnamic acid (CHCA) for the diepoxide or 2,5-dihydroxybenzoic acid (DHBA) for oligomer products as a matrix. Gel permeation chromatography (GPC) of the polymer products was carried out at 75 °C on a Shimadzu LC-10A series apparatus equipped with two PLgel GPC columns (Polymer Laboratories Ltd, the linear range of molecular weight: 200–400,000) and a reflactive index detector. DMF was used as an eluent at a flow rate of 0.5 ml/min. Polystyrene standards with a narrow distribution of molecular weight (M_w: 580–377,400) were used

for molecular weight calibration. Solubility of polymer products was tested by mixing 5 mg of the polymer product with 0.2 ml of solvent. The mixture was shaken at 150 rpm for 24 h at room temperature.

Thermogravimetric analysis (TGA) was conducted with a Perkin Elmer thermogravimetric analyzer TGA 7 at a heating rate of 20 °C/min under a nitrogen atmosphere. Thermal degradation temperature (T_d) was defined as the temperature of the 5% weight loss. Differential scanning calorimetry (DSC) was performed on a Perkin Elmer DSC Pyris 1 under a nitrogen atmosphere. The sample for DSC was weighed (∼10 mg) on a small aluminum pan, followed by sealing the pan. The heat capacity was scanned from −20 to 200 °C at a heating rate of 20 °C/min, and then the sample was cooled to −20 °C at a rate of 20 °C/min. Subsequently, a second heating from −20 to 200 °C at a heating rate of 20 °C/min was carried out. Glass transition temperature (T_g) was taken at the mid-point of the heat capacity change during the second heating process.

3. Results and discussion

3.1. Synthesis of the diepoxide 4 derived from trehalose

The diepoxide 4 derived from trehalose was a white crystal insoluble in most solvent, only soluble in hot DMF and hot NMP. The overall yield from trehalose was about 30%. Fig. 1 shows the ^{1}H NMR spectrum of the diepoxide 4 at 373 K in DMF-d_7. The spectrum revealed that the product was *allo,allo*-isomer according to the literature (Hough et al., 1971). The chemical shifts and the coupling patterns of the peaks correspond to that of *allo,allo*-isomer. The peak corresponding to the 1- and 1′-protons appeared at 5.45 ppm

as a doublet, while that of *manno,manno*-isomer appears as a singlet. Furthermore, the 2- and 2′-protons gave a quartet peak at 3.65 ppm because of couplings between 2-H and 1-H, and between 2-H and 3-H. The elemental analysis data of the product was in good agreement with the calculated values. In the linear-mode MALDI-TOF mass spectrum, the peak of the product appeared at mass/charge 505.7, while the calculated value is 482.5. The value 505.7 is in good agreement with the sum of the calculated value 482.5 and the mass number of sodium atom 23.0. Actually the peak at 505.7 was intensified by addition of trace amount of sodium chloride, which suggests that the detected product was complex of the diepoxide 4 with sodium ion.

3.2. Polymerization of the diepoxide 4 with aliphatic diamine

To evaluate the reactivity of the diepoxide 4 with amine, it was reacted with equimolar amount of aliphatic monoamine, 1-aminotetradecane, at first. The MALDI-TOF MS analysis revealed that the major product was a compound with mass/charge of 697.1, corresponding to the protonated adduct of one diepoxide molecule with one amine molecule (Calcd. 695.9). The reaction did not yield a polymer. Then, the diepoxide 4 was reacted with aliphatic diamine, 1,6-diaminohexane (DAH), in NMP. After the reaction at for 24 h, a soluble polymer ($M_w \sim 6300$) was yielded. However, the solution did not gel and there is no product that has branched chains as far as the result of MALDI-TOF MS. The solubility was assayed and summarized in Table 1. These result implies that the reactivity of the diepoxide 4 is not so high that two epoxy groups could not react with one amino group possibly because of steric hindrance. A similar result is reported in the literature
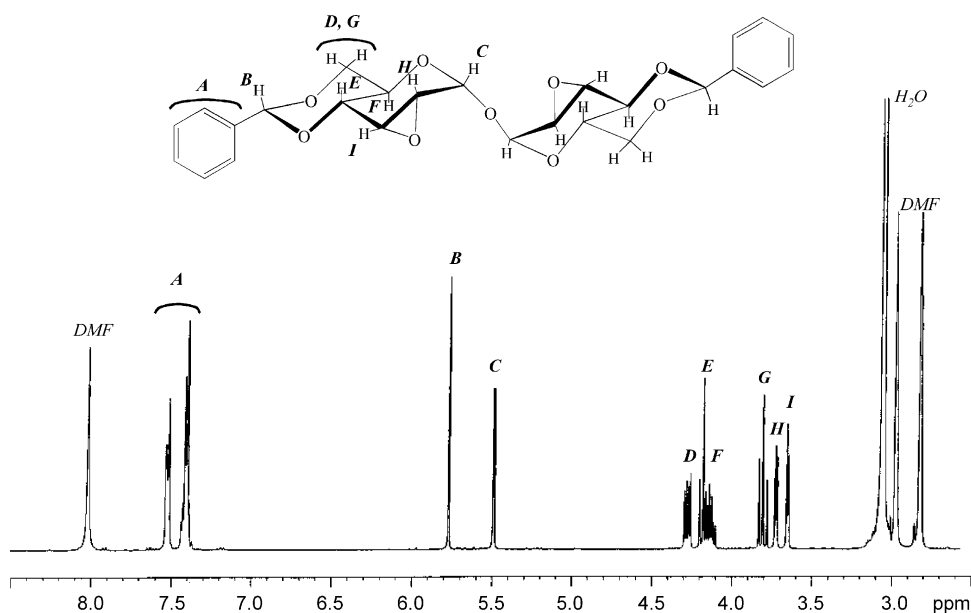

Fig. 1. ^{1}H NMR spectrum of the diepoxide 4.

Table 1
Solubility of polymer products obtained in the reaction of diepoxide **4** with 1,6-diaminohexane (DAH) (A) or *N,N'*-dimethyl-1,6-diaminohexane (DMDAH) (B)

Solvent	Polymer		Solvent	Polymer	
	(A)	(B)		(A)	(B)
Acetone	i	s	Ethyl alcohol	i	i
Chloroform	s	s	Methyl alcohol	i	i
Diethyl ether	i	i	NMP	s	s
DMF	s	s	THF	s	s
DMSO	s	s	Toluene	i	s
Ethyl acetate	i	s	Water	i	i

Five milligrams of the polymer product was mixed with 0.2 ml of solvent. s, soluble; i, insoluble.

involving in the curing of a cyclohexyl epoxide tethered with a cubic silsesquioxane (Choi, Yee, & Laine, 2003). According to our knowledge, sugar-based cationic gemini surfactants (Bell et al., 2003; Fielden et al., 2001; Menger & Keiper, 2000) for nucleic acid transfection as an alternative application can be easily synthesized from the diepoxide **4** by reacting with aliphatic monoamine followed by removing benzylidene groups. The reactivity of the diepoxide **4** is summarized in Fig. 2.

Based on these results, the diepoxide **4** was reacted with *N,N'*-dimethyl-1,6-diaminohexane (DMDAH) which has a higher basicity than DAH to obtain a linear polymer (**5**). Reaction of the diepoxide **4** and DMDAH was carried out at 200 °C. Reaction conditions, yields and molecular weights (GPC) are summarized in Table 2. TPP, TMPP and 2E4MIm were used as a base catalyst, and there is not a serious difference among these catalysts. TPP (10%) showed slightly higher molecular weight than the other catalysts in the 24-h reaction (Table 2). The yield and the M_w increased by increasing reaction time to 48 h. However, the M_n decreased slightly in the 48-h reaction, compared with the 24-h reaction. The decrease of M_n may be due to

Table 2
Polymerization of the diepoxide **4** with DMDAH

Entry	Reaction condition		Yield (%)	Molecular weight (GPC)		
	Time (h)	Catalyst		M_w	M_n	M_w/M_n
1	24	None	69	5 400	2 800	1.9
2	24	5% TPP	68	5 700	3 000	1.9
3	24	10% TPP	74	5 700	3 500	1.6
4	48	10% TPP	83	6 500	2 500	2.6
5	72	10% TPP	69	4 400	2 300	1.9
6	24	10% TMPP	81	4 500	2 900	1.6
7	24	10% 2E4MIm	81	5 100	2 800	1.8

All reactions were carried out at 200 °C in NMP.

slow decomposition of the polymer chain and transacetalization at high temperature (200 °C). The color of the product obtained by the 48-h reaction (Entry 4) was brown, while the product obtained by the 24-h reaction (Entry 3) was slightly brownish white. Furthermore, both M_w and M_n decreased in the 72-h reaction (Entry 5). These results suggest that some side reaction may occur in a long reaction time over 24 h. On the other hand, when the reaction was carried out at 150 °C, the yield and the molecular weight of the product was much lowered (yield 46%, $M_w \sim 3000$, $M_w \sim 2000$). The molecular weight determined by GPC may not represent the actual molecular weight, because the backbone structure of the product **5** differs from that of the polystyrene molecular weight standard. Therefore, the value may represent just relativity. Unlike the diepoxide **4**, the polymer products were soluble in many organic solvents such as chloroform, tetrahydrofuran (THF), toluene, acetone, DMF, and DMSO (Table 1).

Table 3 summarized signals of the MALDI-TOF mass spectrum for the product obtained in the reaction carried out at 200 °C for 24 h in the presence of 10 wt% TPP (Entry 3). The MALDI-TOF mass spectrum also may not reflect
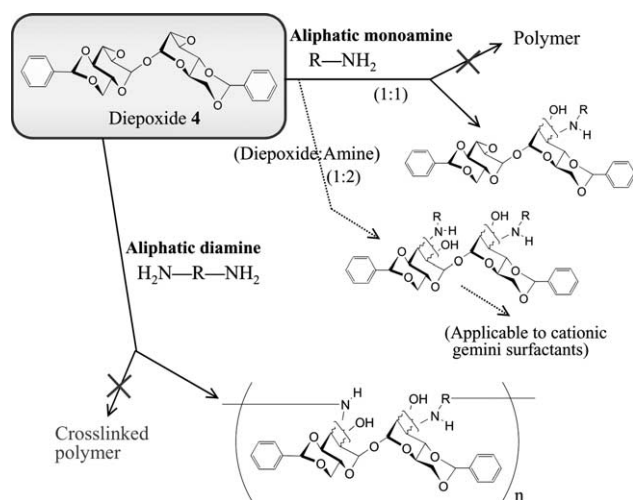

Fig. 2. Schematic representation of the reactivity of the diepoxide **4** with amines.

Table 3
MALDI-TOF mass spectrum (linear mode) analysis of the product **5**

Signal (*m/e*)	Relative intensity	Assignment (diepoxide **4**: DMDAH)	Calculated (*m/e*)
1109.7	43	2:1	1110.2
1254.9	100	2:2	1254.5
1398.3	15	2:3	1398.7
1736.8	14	3:2	1736.9
1879.5	32	3:3	1881.2
2024.8	10	3:4	2025.5
2362.2	14	4:3	2363.7
2506.9	18	4:4	2507.9
2989.0	6	5:4	2990.4
3132.1	6	5:5	3134.7
3615.3	3	6:5	3617.1
3762.3	5	6:6	3761.4
4241.6	3	7:6	4243.9
4383.0	3	7:7	4388.1

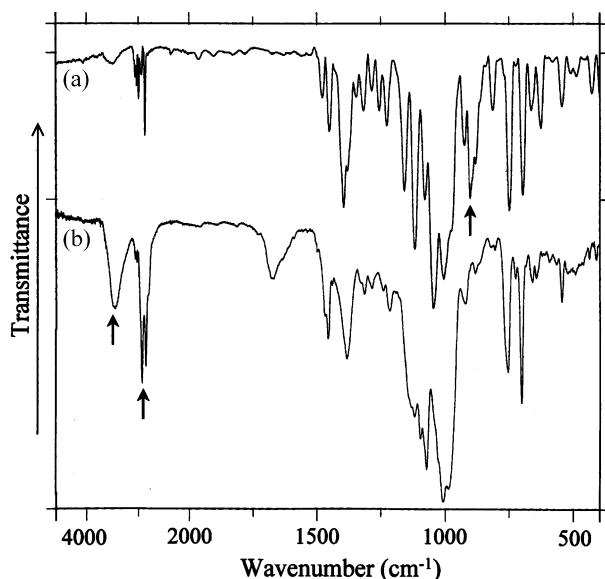The reaction condition corresponds to Entry 3 in Table 2.

Fig. 3. FT-IR spectra of the diepoxide **4** and the polymerization product **5**.

the actual molecular weight dispersion, because molecules became hard to detect as their molecular weights increase. The highest peak of the product was *obs. m/e* 1254.9 (Calcd. 1254.5), which is lower than the M_n determined by GPC analysis. According to the *m/e* values of the product, an epoxy group remained at the end of the oligomer. Differences between the observed mass/charge (*m/e*) and the calculated may be due to the irradiation of the strong laser beam to the sample, which was needed to detect molecules with higher molecular weight.

FT-IR spectrum of the product **5** (Entry 3) was compared with that of the diepoxide **4** in Fig. 3. The absorption peak, which is assigned to the epoxy groups, was observed at $\sim 800\ cm^{-1}$ in the spectrum of the diepoxide **4**. This peak decreased obviously in the product **5**, implying that the epoxy groups were involved in the polymerization. The absorption peak at $\sim 3500\ cm^{-1}$ was assigned to the hydroxyl groups generated by the ring-opening reaction of the epoxy groups. The peaks at $\sim 2950\ cm^{-1}$ were assigned to the methylene and methyl groups of the DMDAH unit. Fig. 4 shows the ^1H NMR spectrum of the product **5** prepared from the diepoxide **4** and DMDAH (Entry 3). The signals at 7.8–7.3 ppm were assigned to the phenyl protons (=C*H*–), 5.7–5.5 ppm to the methine groups ($>$C*H*–) adjacent to the phenyl groups, 5.4–5.2 ppm to the H1 of the trehalose unit, 4.4–3.1 ppm to the methine groups (H2, H3, H4, H5), methylene groups (H6) or hydroxyl protons of the trehalose unit, 3.0–2.6 ppm to the methylene groups adjacent to the nitrogen atom (–C*H$_2$*–N$<$) of the DMDAH unit, 2.5–2.3 ppm to the methyl protons (C*H$_3$*–N$<$) of the DMDAH unit, and 1.6–1.3 ppm to the other methylene protons of the DMDAH units. Complicated peaks appeared at 4.4–3.1 ppm, which correspond to the protons on the glucopyranoside ring, implying that the reaction of the diepoxide **4** with diamine is not regioselective regarding 2- and 3-position.

3.3. Thermal properties of the polymer product (5)

The thermal properties were analyzed by TGA and DSC. Fig. 5 shows the DSC and TGA thermograms for one of the products (Entry 3). The glass transition temperature (T_g) of the products was $\sim 100\ °C$, and the degradation temperature (T_d) was $\sim 320\ °C$ (5% weight loss). No endothermic peak corresponding to crystalline melting was observed in the DSC thermogram, implying that the polymer **5** is amorphous. When the fusion behavior of the oligomer was
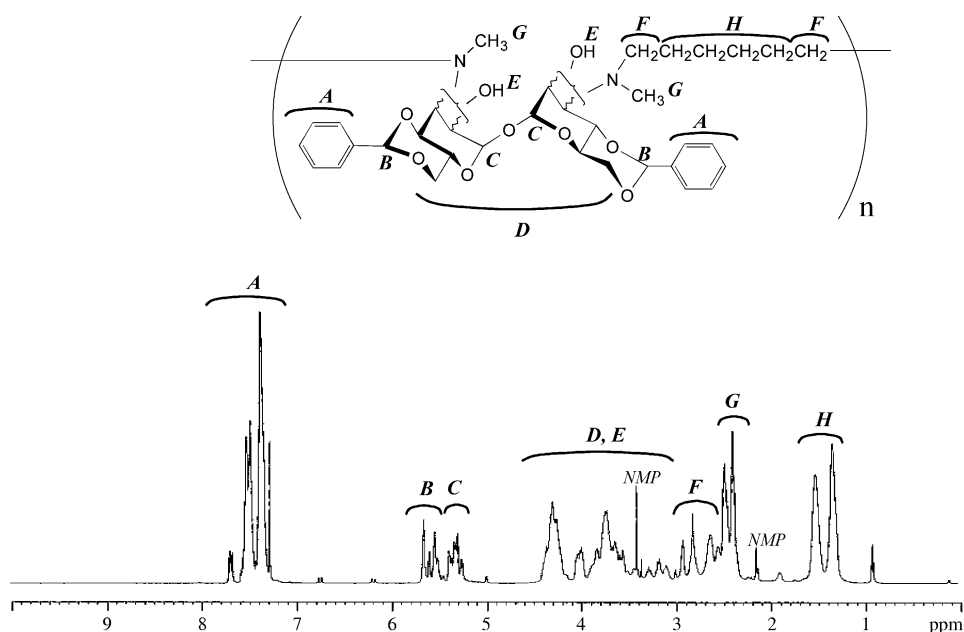

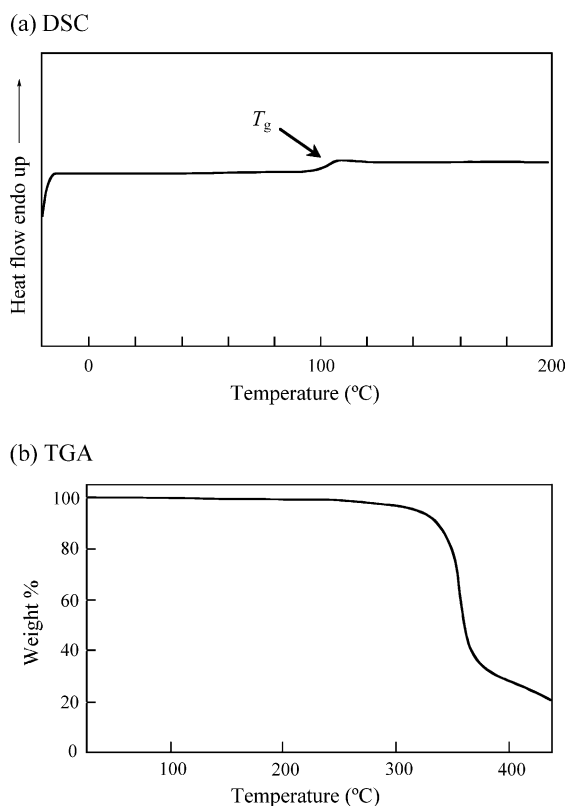Fig. 4. ^1H NMR spectrum of the product **5**.

(a) DSC

(b) TGA

Fig. 5. DSC (a) and TGA (b) thermograms of the product **5**.

observed by a melting point measurement apparatus equipped with a microscope, the fusion began at $\sim 130\,^{\circ}\mathrm{C}$. These results suggest that the product has melt processability.

4. Conclusions

A diepoxide compound derived from trehalose, 2,3-anhyrdo-4,6-O-benzylidene-α-D-allopyranosyl 2,3-anhydro-4,6-O-benzylidene-α-D-allopyranoside, was synthesized and reacted with aliphatic diamines in the presence of a base catalyst. When the ring-opening reaction of the diepoxide compound with 1,6-diaminohexane was carried out, a soluble polymer ($M_w \sim 6300$) was yielded without insoluble matter. The reaction of the diepoxide compound with N,N'-dimethyl-1,6-diaminohexane yielded a linear polymer. The weight average molecular weight (M_w) was ~ 6500 (GPC), when TPP was used as a catalyst. The molecular weight of the product became higher. The product was soluble in many organic solvents such as NMP, DMF, THF, acetone, toluene and ethyl acetate. Thermal analysis with DSC and TGA revealed that the glass transition temperature (T_g) of the polymer was $\sim 100\,^{\circ}\mathrm{C}$ and that the degradation temperature (T_d) was $\sim 320\,^{\circ}\mathrm{C}$, respectively.

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