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Synthesis and Characterization of Crosslinked Hyperbranched Polyglycidol Hydrogel Films

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Hyperbranched polyglycidol (PGLD) was synthesized via anionic ring-opening polymerization of glycidol using a special anionic initiator with multiple initiation sites. The resultant polymers were characterized by ^{1}H and ^{13}C-NMR spectra for confirming their structures, which consisted of linear, hyperbranched and dendritic structures. Molecular weight characteristics were determined by means of the gel permeation chromatography (GPC). With the intention of investigating the possibility of broad applications, PGLD hydrogel films were prepared using various crosslinking agents, i.e., glutaraldehyde and some dicarboxylic acids, and their physical properties such as swelling behavior and tensile (or Young's) modulus were measured and compared.

Keywords hyperbranched polyglycidol, hydrogel film, swelling behavior

Introduction

Much attention has been devoted to the study of glycidol owing to its chemical versatility related to its bifunctional character, namely oxirane ring and hydroxyl group (1–4). Recently, the synthesis of the hyperbranched polyglycidol (PGLD) has gained important notice because of their many advantages. The main advantage of hyperbranched polymers is the ease of their essentially one-step synthesis. More importantly, they have a large number of terminal groups that may have some desirable chemical properties, i.e., as enhanced solubility in some solvent, some catalytic property, etc (5). Among the synthesis methods reported so far, both the anionic (6–8) and cationic (3, 9–11) polymerizations generally lead to well-defined hyperbranched polymers with a large number of branching points and end groups.

In the present study, we prepared linear and hyperbranched PGLD by anionic ring-opening polymerization and investigated the molecular weight characteristics of

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hyperbranched PGLD using gel permeation chromatography (GPC). In addition, we prepared PGLD hydrogel films by using various crosslinking agents such as glutaraldehyde and several dicarboxylic acids. The hydrogel physical properties, including the swelling behavior and tensile (Young's) modulus, were measured and compared with the purpose of potential applications.

Experimental

Materials

Glycidol (Wako Pure Chem., Japan) was distilled under reduced pressure prior to use. Ethyl vinyl ether, sodium, and potassium were also obtained from Wako. Diglycerin was supplied from Kashima Chem., Japan. Acetic acid, p-toluenesulfonic acid, glutaraldehyde, and glutaric acid were also purchased from Wako. Succinic acid and adipic acid were obtained from Kanto Chem., Japan.

Synthesis of Linear Polyglycidol

Synthesis of 1-Ethoxy Ethyl Glycidyl Ether. 1-Ethoxy ethyl glycidyl ether (EEGE) was obtained in the reaction of glycidol (GLD) with ethyl vinyl ether, catalyzed with p-toluenesulfonic acid (p-TsOH). Glycidol and ethyl vinyl ether were placed in a two-necked flask. p-TsOH, dissolved in chloroform, was added under stirring at ambient temperature until no heat evolved. After evaporation of ethyl vinyl ether and chloroform, the p-TsOH was removed under reduced pressure. Next, unreacted glycidol was precipitated in n-hexane and removed. Consecutively, after n-hexane was removed by evaporation, the water was evaporated under reduced pressure. The purity of the product was checked by ^{1}H and ^{13}C-NMR spectra: ^{1}H-NMR: δ_H (D_2O, ppm) 4.75 (CH); 3.9–3.4 (CH_2); 3.15 (CH); 2.8–2.6 (CH_2); 1.35 (CH_3); 1.2 (CH_3). ^{13}C NMR: δ_C (D_2O, ppm) 100 (CH); 65 (CH_2); 61 (CH_2); 51 (CH); 45 (CH_2); 20 (CH_3); 16 (CH_3).

Synthesis of Poly(1-ethoxy ethyl glycidyl ether)

Initiator. Two kinds of initiators, sodium ethoxide (NaOEt) and potassium ethoxide (KOEt), were used for the polymerization. Sodium was placed in a two-necked flask fitted with argon inlet and dried up. The distilled ethanol was added under stirring for 1 h at ambient temperature. Unreacted ethanol was removed by evaporation, providing sodium ethoxide catalyst. Potassium ethoxide catalyst was made in a similar manner.

Anionic Polymerization. In a two-necked flask containing the resulting metal alkoxides (NaOEt and KOEt) charged with argon, EEGE was added under stirring and the reaction was conducted at 120°C. The anionic polymerization was initiated by metal alkoxides. The reaction was terminated by adding excess methanol, with the methanol subsequently removed by evaporation. The products were analyzed using ^{1}H and ^{13}C-NMR spectroscopes: ^{1}H-NMR: δ_H (D_2O, ppm) 4.7 (CH); 3.8–3.4 (CH_2); 1.3 (CH_3); 1.15 (CH_3). ^{13}C-NMR: δ_C (D_2O, ppm) 99.5 (CH); 78.5 (CH_2); 70 (CH_2); 65 (CH_2); 61 (CH_2); 20 (CH_3); 15 (CH_3).

GPC (THF): $M_n = 7470$ $gmol^{-1}$; $M_w = 10980$ $gmol^{-1}$; $M_w/M_n = 1.47$ (where M_n, M_w, and M_w/M_n are number-average, weight-average molecular weight, and polydispersity index, respectively).

Synthesis of Linear Polyglycidol by Hydrolysis of PEEGE

Linear PGLD, which can be prepared by hydrolysis of PEEGE. PEEGE was hydrolyzed using acid catalyst, wherein two kinds of acid catalysts (acetic acid and p-TsOH) were used. First, the hydrolysis reaction with acetic acid as an acid catalyst was as follows. PEEGE was placed in a flask and the mixture of 5 vol% acetic acid aqueous solution and methanol/acetone solvent mixture (1 : 1, v/v) were added with stirring for 12 h. After evaporating the solvent, acetic acid was removed by precipitation in n-hexane. Then, the products were obtained after evaporating n-hexane. Secondly, the hydrolysis reaction with p-TsOH, as an acid catalyst, was as follows. PEEGE was dissolved in the solvent mixture of acetone, ethanol, and water (1 : 1 : 1, v/v/v). p-TsOH was added into the solution, and the reaction mixture was stirred at 80°C until water was completely removed. Then, the linear PGLD was obtained and analyzed using ^{13}C-NMR spectroscopy.

Synthesis of Hyperbranched Polyglycidol

Initiator. A two-necked flask was charged under nitrogen with sodium, followed by distilled ethanol added cautiously. The reaction mixture was stirred at ambient temperature until the sodium completely reacted. A solution of diglycerin in distilled ethanol was added, and then heated at 120°C under reduced pressure. After removing ethanol, the initiator was obtained.

Anionic Polymerization. A typical polymerization procedure was as follows. In a two-necked flask, the initiator was taken under argon atmosphere and heated up to 120°C. Glycidol was added at a rate of 1 ml/min with stirring and the polymerization was initiated. After the completion of polymerization, the unreacted glycidol was removed after stirring for 30 min at 120°C under reduced pressure. The hyperbranched PGLD was obtained as a viscous syrup. The products were analyzed using ^{13}C-NMR spectroscopy.

Crosslinking of Polyglycidol and Preparation of Polyglycidol Hydrogel Film

The PGLD hydrogel films were prepared by crosslinking with various crosslinking agents such as glutaraldehyde, succinic acid, glutaric acid, and adipic acid. To an aqueous solution in which crosslinking agent and polymer were dissolved with various mole ratios of [-COOH] or [-COH] of crosslinking agent to [-OH] of PGLD, p-TsOH was added as an acid catalyst. The above solution was cast on polyethylene substrate and covered with Teflon sheet. Then, the solution was dried by heating at 70°C. At higher concentrations of crosslinking agent, PGLD hydrogel films could not be obtained.

Measurements

^{1}H and ^{13}C-NMR spectroscopy was used for structural characterization of the products. ^{1}H and ^{13}C-NMR spectra were obtained at 400 MHz on a Bruker DPX-400 using D_2O as solvent. Molecular weight characteristics of PGLD polymers prepared were estimated by gel permeation chromatography (GPC), based on the calibration with polyethylene glycol standard. The water was used as the mobile phase at a flow rate of 0.5 ml/min. The gel fraction of PGLD hydrogel film was determined as a measure of the degree of

gelation by extraction with distilled water. The resultant PGLD hydrogel films obtained via a crosslinking reaction were weighted after drying. They were then immersed in distilled water and extracted. After subsequent drying, extracted samples were weighed. The gel fraction was calculated using the following relationship:

$$\text{Gel fraction } (\%) = \frac{W}{W_0} \times 100$$

where W_0 and W were the weights of dried sample before extraction and after extraction. The water content of the PGLD hydrogel films after swelling was examined as follows (12, 13). The samples were immersed in distilled water. The sufficiently swollen films were weighed. After drying, the samples were re-weighed. The equilibrium degree of swelling was then calculated according to the following equation:

$$\text{Equilibrium degree of swelling } (\%) = \frac{(W_s - W_d)}{W_d} \times 100$$

where W_d and W_s denote the weights of dried and swollen PGLD hydrogel films, respectively. The initial tensile (or Young's) modulus of the hydrogel films was measured using thermal mechanical analysizer (TMA) in the tension mode. Strip-shaped specimens with dimensions of 20 × 3.5 mm and thickness of around 1.2 mm were used for the tensile test at an extension rate of 50 mm/min at 15°C. The Young's modulus was measured in a static mode.

Results and Discussion

The polymerization of glycidol was carried out with and without protection of the hydroxyl groups of glycidol. In order to obtain the linear PGLD, the hydroxyl group of the monomer has to be protected before its polymerization because functional groups with relatively acidic hydrogen would normally participate in chain transfer reaction in the anionic polymerization and thus lead to the irregular structures. In this study, linear PGLD was obtained after cleavage of the acetal protecting group of the EEGE units. PEEGE was obtained by the anionic ring-opening polymerization of EEGE initiated with NaOEt and KOEt at 120°C. Subsequently, the acetal groups of PEEGE were converted into hydroxyl groups by hydrolysis in the presence of acid catalyst, leading to the desired PGLD with linear 1,3 structure. The molecular weights of linear PGLD, as determined by GPC, were in the range of 2000 ~ 5000, which is about half of the molecular weight of PEEGE, and linear PGLDs have narrow polydispersities around 1.3, as summarized in Table 1. The ^{13}C-NMR spectrum of the linear PGLD shows three well-resolved peaks between 60 and 80 ppm. In this ^{13}C-NMR spectrum, the characteristic peaks of PEEGE disappeared, which means that PEEGE was converted to PGLD by hydrolysis. Three signals due to linear 1,3 structure appear at 69 ppm (CH_2 carbon, a), 79.7 ppm (CH carbon, b), and 60.9 ppm (CH_2OH carbon, c), as shown in Figure 1.

The direct anionic ring-opening polymerization of unprotected glycidol yields highly branched polymers. The incorporation of the anionic initiator with four initiation sites synthesized using diglycerin and sodium in this study can produce hyperbranched polymer structures, with the number of arms corresponding to the functionality of the initiator. When branches have further branches the resultant PGLD can eventually have a nearly spherical molecular structure, close to a dendritic structure with a high concentration of surface end groups. The molecular weights of hyperbranced PGLD were relatively low

Table 1
Molecular weight characteristics of PEEGE and linear PGLD

Sample	Mole ratio [EEGE]/[initiator]	PEEGE		PGLD	
		M_n	M_w/M_n	M_n	M_w/M_n
PGLD 1	50	3470	1.36	1600	1.20
PGLD 2	200	7470	1.47	3240	1.34
PGLD 3	300	9060	1.80	2160	1.48
PGLD 4	400	11470	1.57	3250	1.32
PGLD 5	500	16140	1.74	4620	1.52
PGLD 6	400	6790	1.75	2550	1.32
PGLD 7	200	4670	2.45	2290	1.65

($M_n = 1100 \sim 1800$) because of the fact that initiation occurs rapidly in competition with propagation and due to the presence of chain transfer reaction to the monomer in the system. Rather narrow molecular weight distributions below 2.0 were achieved by slow monomer addition conditions (Table 2). Examination by ^{13}C-NMR spectrum of the hyperbranched PGLD indicated that its structure was much more complex than that of linear PGLD due to a large variety of possible branched structures, as shown in Figure 2. The resulting hyperbranched PGLD possesses structures composed of the linear units, branched and dendritic units as well as end groups (Scheme 1). The signal analysis in the ^{13}C-NMR spectrum of the resulting PGLD was conducted with reference to information suggested by Vanderberg (6) and other (9, 14).

In the anionic ring-opening polymerization of unprotected glycidol, two different propagating species lead to two types of repeating units. When the secondary hydroxyl group has propagated, the linear 1,3 structure (L_{13}) with -CH_2-CH(CH_2OH)-O- repeating unit is generated: CH_2OH carbon at 60.6 ppm (f), CH_2 carbon at 69 ppm (d), and CH carbon at 79 ppm (e). When the primary hydroxyl group formed after the intramolecular proton

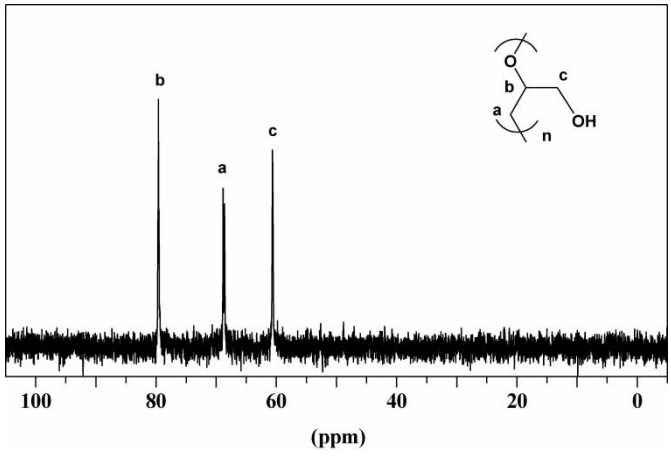


Figure 1. ^{13}C-NMR spectrum of linear polyglycidol.

Table 2
Polymerization conditions and molecular weight characteristics of hyperbranched PGLD

Sample	Mole ratio [GLD]/[Initiator]	M_n	M_w/M_n	Conversion (%)
PGLD 8	50	1120	1.93	>99
PGLD 9	200	1270	1.72	>99
PGLD 10	400	1420	3.21	>99
PGLD 11	167	1770	2.05	>99

transfer has undergone propagation, the corresponding linear 1,4 structure (L_{14}) composed of -CH_2-CHOH-CH_2-O- repeating units is formed: both CH_2 carbons at 72 ppm (g,i) and CHOH carbon at 68.5 ppm (h). When both hydroxyl groups have reacted with the monomer, the hyperbranched and dendritic units are introduced with the CH carbon at 78 ppm. However, if no monomers are added, the terminal units are formed at the chain ends. The corresponding ^{13}C-NMR chemical shift of end groups (-CH_2-CHOH-CH_2OH) is at 62 ppm related with CH_2OH carbon.

The high degree of hydroxyl group of hyperbranched PGLD makes their crosslinking possible (Scheme 2). Glutaraldehyde and various dicarboxylic acids such as succinic acid, glutaric acid, and adipic acid were used as crosslinking agents and p-TsOH was used as catalyst. In the case of using glutaraldehyde as a crosslinking agent, the crosslinking reaction proceeded well without the aid of heating when acid catalysts, p-TsOH or HCl, were used. However, the degree of crosslinking with heating was higher than that without heating, due to the effect of reducing the side reaction of glutaraldehyde with

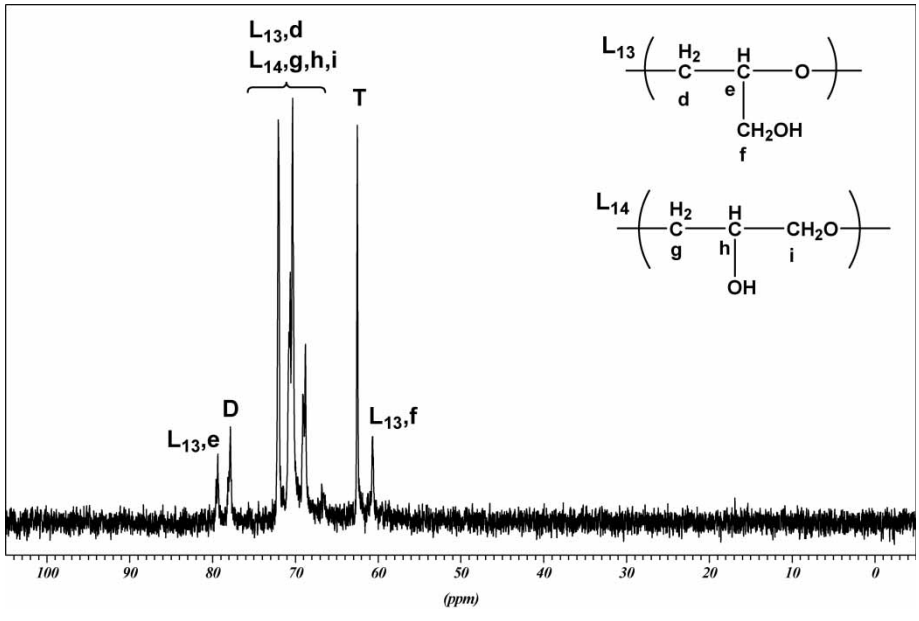
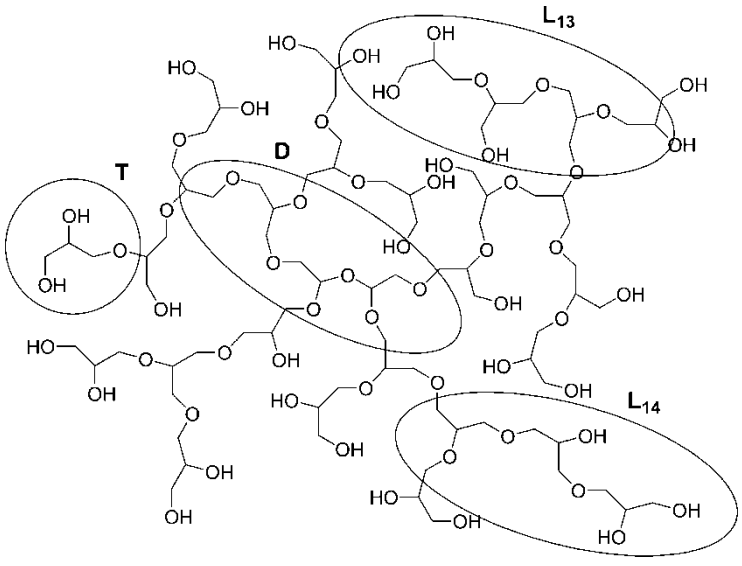


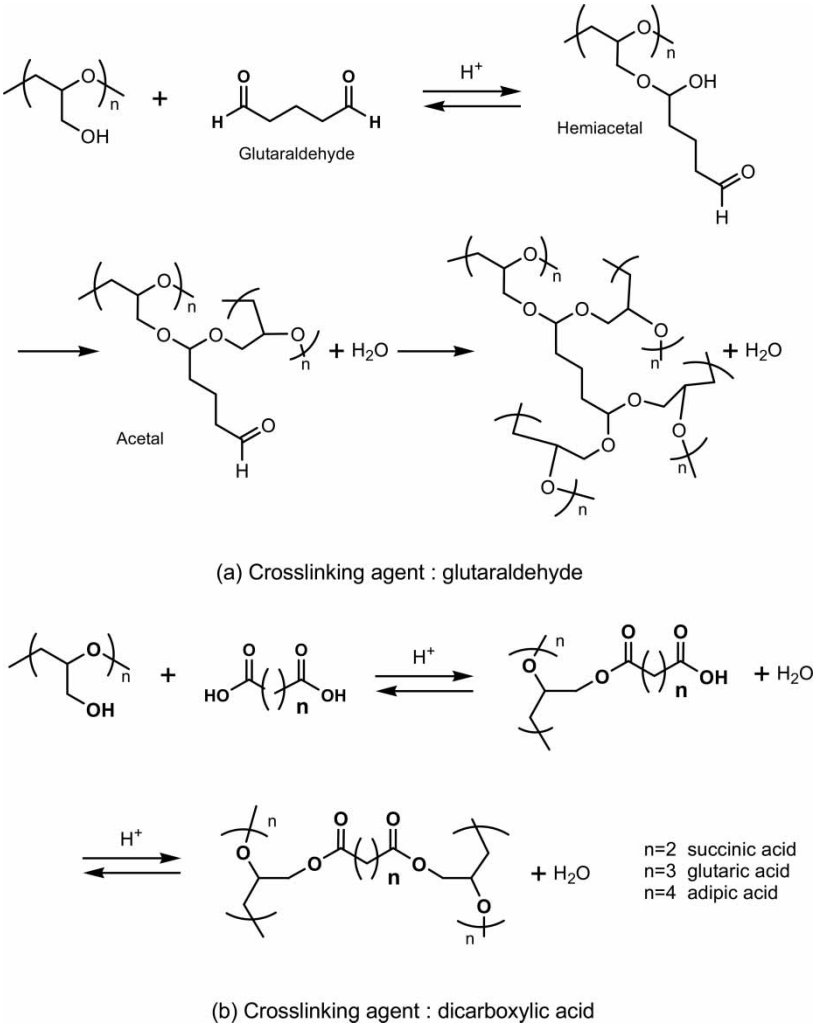
Figure 2. ^{13}C-NMR spectrum of hyperbranched polyglycidol.



Scheme 1. Schematic architecture of hyperbranched polyglycidol.

acid catalyst. An aldehyde group of glutaraldehyde reacts with the hydroxyl group of PGLD in the presence of acid catalyst, and then the hemiacetal is formed. The hemiacetal reacts with a second PGLD, leading to the formation of the acetal. Meanwhile, when using aforementioned dicarboxylic acids as the crosslinking agent, the heating process was prerequisite to the crosslinking. When succinic acid and glutaric acid were used as the crosslinking agent, it was chemically crosslinked without an additional acid catalyst because of acting themselves as acid catalyst, but the degree of crosslinking was less than that with acid catalyst. The preparation of PGLD hydrogel films was accomplished by the abovementioned crosslinking method using difunctional crosslinking agents in the presence of p-TsOH at 70°C. The resultant PGLD hydrogel films had no bubbles and were transparent and homogeneous, yielding moderate mechanical strength.

Table 3 provides information on the gel fraction (and hence, degree of gelation) and the swelling behavior of the PGLD hydrogel films prepared at various crosslinking agent concentrations. Figure 3 shows the effects of concentration of crosslinking agent on the gel fraction and swelling of PGLD hydrogel films crosslinked with glutaric acid. PGLD hydrogel films exhibited relatively higher degree of swelling even at low concentrations of crosslinking agent. This can be attributed to the strong hydrogen bonding between the abundant hydroxyl groups of PGLD and water, thereby resulting in the increase of the hydrophilicity, as well as the formation of the three-dimensional network structure via crosslinking. This makes it possible to retain a considerable amount of water. As the concentration of crosslinking agent increases, all samples showed an increase in the gel fraction, whereas the degree of swelling of PGLD hydrogel film decreased. This may arise because the increase of concentration of crosslinking agent resulted in the increase of crosslinking density, which severely limits the possibility of the solvent penetration into the network. The branched structure of PGLD also affected the swelling behavior of the resulting films. When the concentration of crosslinking agent was 7.5 mol%, the hydrogel film prepared with linear PGLD had a similar value of gel fraction in comparison with the hydrogel film from hyperbranched PGLD, but the



Scheme 2. Mechanism of crosslinking of PGLD with various crosslinking agents.

degree of swelling of linear PGLD film was two times as high as that of hyperbranched PGLD film. Two factors may be responsible for these results. Considering that the molecular weight of linear PGLD was higher than that of hyperbranched PGLD in our results (see Tables 1 and 2), linear PGLD hydrogel films with higher molecular weight will provide more sites for the crosslinking, that is, the number of crosslinking points per one polymer chain will increase with the increasing molecular weight. Moreover, when compared to linear PGLD films with the similar molecular weight, many branches of hyperbranched PGLD films give rise to enhance dense interior structures, and therefore hyperbranched PGLD films exhibited somewhat lower water contents. When the concentration of crosslinking agent was more than 75 mol%, the gel fraction of linear PGLD film was higher than that of hyperbranched PGLD film, leading to the decrease of degree of swelling, but it did not show any marked differences in the values. This may be due to the dense spherical structure of hyperbranched PGLD

Table 3
The gel fraction and equilibrium degree of swelling of PGLD hydrogel films

Crosslinking agent	PGLD	[-COH]/[-OH] or [-COOH]/[-OH]	Gel fraction (%)	Equilibrium degree of swelling (%)
Glutar aldehyde	PGLD 3	0.075	66.1	611
		0.15	94.0	101
		0.25	87.2	92
	PGLD 11	0.075	69.7	330
Succinic acid	PGLD 7	0.075	87.4	419
		0.25	95.5	144
Glutaric acid	PGLD 3	0.075	84.0	543
		0.25	95.6	116
		0.45	91.9	60
	PGLD 7	0.75	94.7	26
		1.50	90.6	14
	PGLD 11	0.25	86.4	170
Adipic acid	PGLD 7	0.075	83.7	242

compared to linear PGLD, resulting in difficulties of crosslinking. As a whole, even at low concentrations of crosslinking agent, the PGLD hydrogel films proved to swell 500 times higher than that in their dry state.

The values of the (initial) Young's modulus for PGLD hydrogel films crosslinked with glutaric acid and glutaraldehyde were evaluated from the slope of the stress-strain curve and are displayed in Table 4 and Figure 4 as a function of concentration of crosslinking agent.

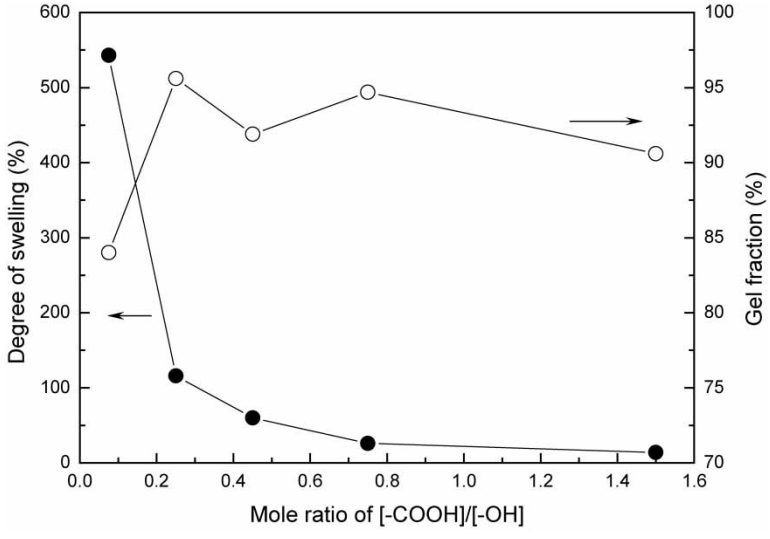


Figure 3. Effect of concentration of crosslinkig agent on the gel fraction and swelling of PGLD hydrogel films crosslinked with glutaric acid.

Table 4
The Young's modulus of PGLD hydrogel films

Crosslinking agent	PGLD	[-COH]/[-OH] or [-COOH]/[-OH]	Young's modulus (MPa)
Glutar aldehyde	PGLD 3	0.075	0.15
		0.15	5.68
		0.25	7.64
Succinic acid	PGLD 7	0.25	3.04
Glutaric acid	PGLD 3	0.075	0.16
		0.25	3.43
	PGLD 7	0.75	15.48
		1.50	19.70
	PGLD 11	0.25	4.02
Adipic acid	PGLD 7	0.075	1.86

The values of observed Young's modulus suggest that a significant stiffening of the structure has been attained even at low concentrations of the crosslinking agent for two kinds of hydrogel films, which was ascribed to both the increases in the extent of covalent crosslinks and the enrichment of hydrogen bonding involved. The Young's modulus increased with the increasing concentration of crosslinking agent for all the crosslinking agents employed in our study, with some definite differences in magnitude among them. It was also found that the Young's modulus of hyperbranched PGLD film was higher than that of linear PGLD film at the same concentration of crosslinking agent. This may be attributable to

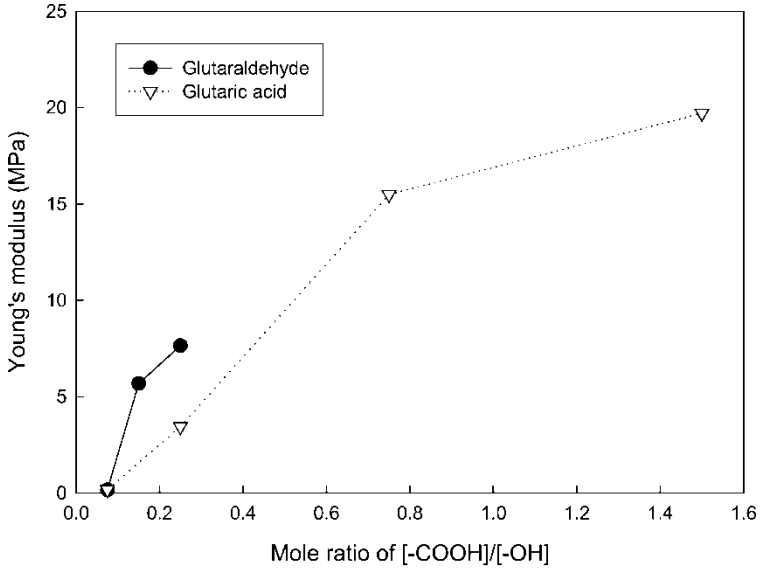


Figure 4. The Young's modulus of PGLD hydrogel films crosslinked with glutaraldehyde and glutaric acid as a function of concentration of crosslinking agent.

the presence of the highly branched structure of hyperbranched PGLD in addition to three-dimensional network structure via crosslinking as compared to linear PGLD.

Conclusions

Hyperbranched polyglycidol (PGLD) was synthesized by direct anionic ring-opening polymerization of unprotected glycidol using a tetrafunctional anionic initiator. Examination by ^{13}C-NMR spectroscope indicates that hyperbranched PGLD has an extensive branched structure similar to a dendritic structure. It is worth noting that according to our simple synthetic route, PGLD hydrogel films can be prepared via crosslinking reaction of linear and hyperbranched PGLD with glutaraldehyde and various dicarboxylic acids. The resultant PGLD hydrogel films exhibited higher degree of swelling ($\sim$500%) even at lower concentrations of the crosslinking agent used. The (initial) Young's modulus of the PGLD hydrogel films was also increased by crosslinking, implying the enhancement of stiffness of the structure in films via crosslinking. Both the great affinity for water and the increase in the Young's modulus even at low crosslinker concentrations can indeed make hyperbranched PGLD hydrogel films eligible for a number of applications.

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