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POLYMERIZATION OF ACRYLATE MONOMER CONTAINING TWO HYDROXY GROUPS INITIATED WITH SODIUM HYDRIDE FOR SYNTHESIS OF HYPERBRANCHED POLYMER

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ABSTRACT

Hyperbranched polymer **2b** was synthesized by the proton-transfer polymerization of an acrylate monomer **1b** containing two hydroxy groups. The polymerization was carried out in the presence of sodium hydride as an initiator at $80-100°C$. The analytical data of the product supported the structure of polyester-ether **2b**, obtained by the Michael-type addition, followed by the proton-transfer process. The values of the degree of branching were determined by the methanolysis experiment of the product polymers, which were in the range of $0.5-0.6$. The highest molecular weight determined by GPC analysis was 7600. The molecular weight increased further after the quantitative consumption of the monomer, indicating the occurrence of the reaction between the polymer and the polymer.

Key Words: Hyperbranched polymer; Proton-transfer polymerization; Acrylate monomer; Michael addition

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INTRODUCTION

Hyperbranched polymers, macromolecules with branched backbones, have recently attracted much attention due to their specific structures and their different properties compared to the linear analogues. The preparation of these polymers was mainly conceived as an extension of a well-known class of polymers, in which hyperbranched polymers are typically prepared by the step-growth polymerization of AB_x-type monomers.[1] Another way to achieve hyperbranched polymers is the chain-addition polymerization of monomers containing both an initiating function and a propagating function in the same molecules.[2] This type of chain-addition polymerization yields hyperbranched polymers as products of multiple polymerization reactions within one polymer molecule. Here, the polymerization reactions are initiated by both an added initiator and initiating functional groups which are present in the monomers. The different type of chain polymerization for the preparation of the hyperbranched polymers was achieved by ring-opening polymerization of cyclic carbamates via π-allylpalladium complex, termed "multibranching polymerization".[3] During the polymerization, the number of propagating ends increased with the progress of the polymerization, and consequently, hyperbranched dendritic polymers were produced. Recently, we have reported that triphenylphosphine-initiated proton-transfer polymerization of acrylate monomer **1a** containing two hydroxy groups gave the hyperbranched polymer **2a** (Sch. 1).[4] The polymerization provided the new method for the synthesis of hyperbranched polymers by the chain-growth type polymerization. The product polymers, however, sometimes contained the insoluble fractions, and the molecular weights of the soluble fractions were always low. Furthermore, the side reaction catalyzed by triphenylphosphine, as shown in Sch. 2, took place during the polymerization to give the unexpected polymer unit **3**.[5] Therefore, to obtain the soluble hyperbranched

1a; R = CH$_3$
1b; R = CH$_2$OBn

2a; R = CH$_3$
2b; R = CH$_2$OBn

initiator = Ph$_3$P, NaH

Bn = −CH$_2$−
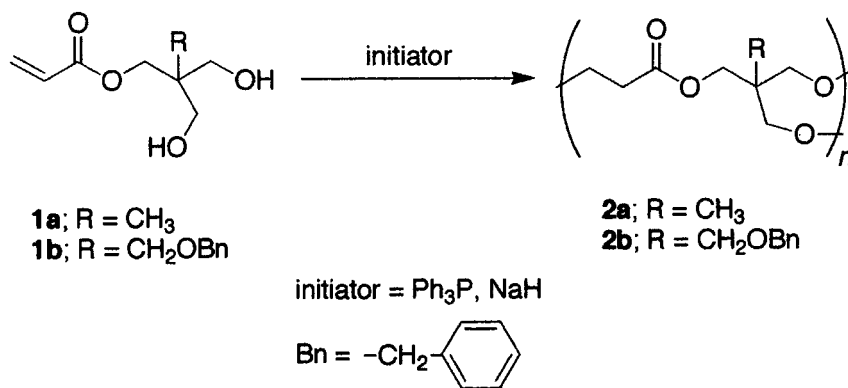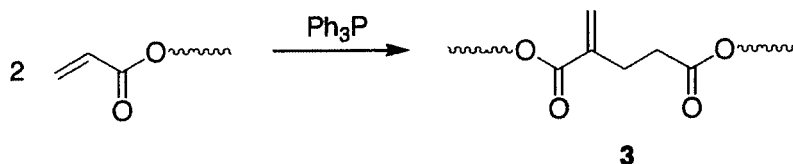
Scheme 1.

Scheme 2.

polymers with the higher molecular weights and suppress such side reactions, we have examined the present type of proton-transfer polymerization using other monomers and initiators. As a result, monomer **1b,** having the bulky substituent, has been polymerized by sodium hydride initiator, giving rise to the soluble hyperbranched polyester-ether with relatively high molecular weight, which exclusively consists of the unit **2b**. In this paper, we report the proton-transfer polymerization of **1b** initiated with sodium hydride to produce the hyperbranched polymer **2b**.

EXPERIMENTAL

Materials

Sodium hydride of the initiator was used as a 60% dispersion form in mineral oil. Solvents were purified by distillation. Other reagents were used as received.

Synthesis of Monomer 1b

Monomer **1b** was synthesized from pentaerythritol. Under argon, pentaerythritol (40.8 g, 0.300 mol) and sodium hydride (60% dispersion in mineral oil, 14.4 g, 0.360 mol) were dispersed in DMF (100 mL) and the solution was heated at 50°C. Into the suspension with stirring, a solution of benzyl bromide (35.7 mL, 0.300 mol) in DMF (50.0 mL) was added dropwise over 2 h at 50°C and the mixture was stirred further for 1 h at that temperature. After the reaction mixture was cooled to room temperature and a small amount of methanol was added, the solution was concentrated by evaporation in vacuo. The residue was diluted with water and the water solution was extracted successively with toluene and ethyl acetate. The ethyl acetate extract was dried over Na_2SO_4, filtered, and evaporated to give a crude monobenzylated triol (ca. 12.4 g, 0.0549 mol). To a solution of the triol (12.4 g, 0.0549 mol), hydroquinone (radical inhibitor, 0.0300 g, 0.275 mmol), and triethylamine (9.20 mL, 0.0660 mol) in THF (36.5 mL), a solution of acryloyl chloride (4.50 mL, 0.0550 mol) in THF (36.5 mL) was added dropwise over 45 min at 50°C with stirring under argon. The mixture was stirred further for 1 h at that temperature and cooled to room temperature. The precipitated

salt was filtered off and the filtrate was concentrated by evaporation. Diethyl ether was added to the residue and the insoluble fraction was separated by filtration. The filtrate was evaporated in vacuo and the residual material was purified by column chromatography on silica gel with ethyl acetate/cyclohexane (1/1) to give monomer **1b** (3.37 g, 0.0120 mol, 4.0% yield). ^{1}H NMR (CDCl$_3$): δ 2.67 (br s, 2H, OH), 3.50 (s, 2H, CH$_2$OBn), 3.61–3.69 (2d, 4H, C*H$_2$*OH), 4.31 (s, 2H, CH$_2$OC=O), 4.52 (s, 2H, CH$_2$Ph), 5.83–6.46 (m, 3H, CH$_2$=CH-), 7.28–7.35 (m, 5H, C$_6$H$_5$). IR (neat, cm^{-1}): 1738 (C=O).

Polymerization

A typical procedure was as follows (entry 4). Under argon, monomer **1b** (0.140 g, 0.50 mmol), sodium hydride (60% dispersion in mineral oil, 0.00660 g 0.15 mmol), and a small amount of hydroquinone monomethyl ether (radical inhibitor) were charged in a polymerization tube. The tube was sealed, and heated at 100°C for 72 h. After the tube was cooled to room temperature, the resulting mixture was dissolved in chloroform (5.0 mL). The solution was washed with saturated NaCl water twice, dried over Na$_2$SO$_4$, filtered, and evaporated. The concentrated solution was poured into petroleum ether (100 mL) to precipitate a polymer. The polymeric material was isolated by decantation and dried under reduced pressure to give **2b** (0.110 g) in 75.1% yield.

Methanolysis of 2b

Under argon, polymer **2b** (0.110 g) was dissolved in THF (5.0 mL) and a solution of sodium methoxide (0.0210 g, 0.390 mmol) in methanol (7.0 mL) was added. After the mixture was stirred for 3 days at room temperature, it was treated with cation exchange resin (Dowex 50W-X8), evaporated, and dried in vacuo to give the methanolysis products. For the analytical samples, the products were separated by column chromatography on silica gel with ethyl acetate/cyclohexane (1/2 for **4**, 1/1 for **5** and **6**). ^{1}H NMR of **4** (CDCl$_3$): δ 2.55 (t, J = 6.0 Hz 4H, CH$_2$C=O), 3.46 (s, 2H, CH$_2$OBn), 3.48 (s, 4H, C*H$_2$*CH$_2$C=O), 3.64–3.71 (m, 12H, CH$_3$, C*H$_2$*OH, and C*H$_2$*OCH$_2$CH$_2$C=O), 4.49 (s, 2H, OCH$_2$Ph), 7.31–7.32 (m, 5H, C$_6$H$_5$). ^{1}H NMR of **5** (CDCl$_3$): δ 2.56 (t, J = 6.0 Hz 2H, CH$_2$C=O), 3.50 (s, 2H, CH$_2$OBn), 3.55 (s, 2H, C*H$_2$*CH$_2$C=O), 3.64–3.68 (m, 9H, CH$_3$, C*H$_2$*OH, and C*H$_2$*OCH$_2$-CH$_2$C=O), 4.50 (s, 2H, OCH$_2$Ph), 7.21–7.38 (m, 5H, C$_6$H$_5$). ^{1}H NMR of **6** (CDCl$_3$): δ 3.51 (s, 2H, CH$_2$OBn), 3.73 (s, 6H, C*H$_2$*OH), 4.51 (s, 2H, OCH$_2$Ph), 7.28–7.36 (m, 5H, C$_6$H$_5$).

Measurements

^{1}H (500 MHz) and ^{13}C (50 MHz) NMR spectra were recorded using Varian INOVA 500 and Mercury 200 spectrometers, respectively. IR spectra were recorded using a HORIBA FT-200 spectrometer. GPC analyses were performed by using a HITACHI L-7100 with an RI detector under the following conditions: TOSOH TSKgel G5000H$_{XL}$ column with DMF containing 0.02 mol/L as eluent at a flow rate of 1.0 mL/min.

RESULTS AND DISCUSSION

The polymerization of **1b** was carried out with sodium hydride as an initiator in the presence of hydroquinone monomethyl ether as an radical inhibitor at $80-100°$C. The product was isolated as an insoluble fraction in petroleum ether, which was soluble in such solvents as chloroform, DMF, and THF, but insoluble in lower polar solvents like hydrocarbons, as well as water. The polymer structure was identified by means of ^{1}H NMR, ^{13}C NMR, and IR spectroscopy. Fig. 1(a) shows the ^{1}H NMR spectrum of the polymer dissolved in CDCl$_3$. A new peak **a** at δ 2.48 assigned to the $CH_2C(C=O)O$ group appears (2H) compared to the ^{1}H NMR spectrum of **1b**, indicating that the reaction proceeded by a Michael-type addition followed by a proton-transfer process giving a polyester-ether. Other peaks are also assignable to the structure of polyester-ether as indicated in Fig. 1(a). The intensity of the peaks **f** at δ $5.74-6.40$ due to the acrylate end group is very low compared to the peaks of the polymer chain, indicating the high degree of polymerization of the product polymer. When the polymerization of **1b** was carried out using triphenylphosphine as the initiator, two peaks at δ 5.61 and 6.20 appear beside the peaks due to acrylate end group, as shown in Fig. 1(b). These two peaks are ascribed to the α-substituted acrylate group, which was formed by the dimerization of the acrylate end groups of the polymer catalyzed by triphenylphosphine (Sch. 2). In the ^{1}H NMR spectrum of the polymer obtained using sodium hydride as the initiator, such a pair of the peaks has not been observed (Fig. 1(a)), indicating that the side reaction did not take place during the polymerization. The ^{13}C NMR spectrum of the same sample in Fig. 2 exhibits a peak **a** at δ 34.8 assigned to $CH_2C=O$, peaks **b** at δ $43.5-45.0$ ascribed to $C(CH_2\text{-})_4$, peaks **c** at δ $63.2-73.6$ due to CH_2O, peaks **d** at δ $127.3-138.1$ ascribed to C_6H_5, and peaks **e** at δ $171.5-172.0$ assigned to C=O. The peaks due to the acrylate end group are too small to be detected by the ^{13}C NMR spectrum. The IR spectrum of the polymer displayed strong absorption at 1734 cm^{-1} attributable to $\nu_{C=O}$ of the ester groups. These analytical results strongly suggest that the product polymer has a polyester-ether structure.
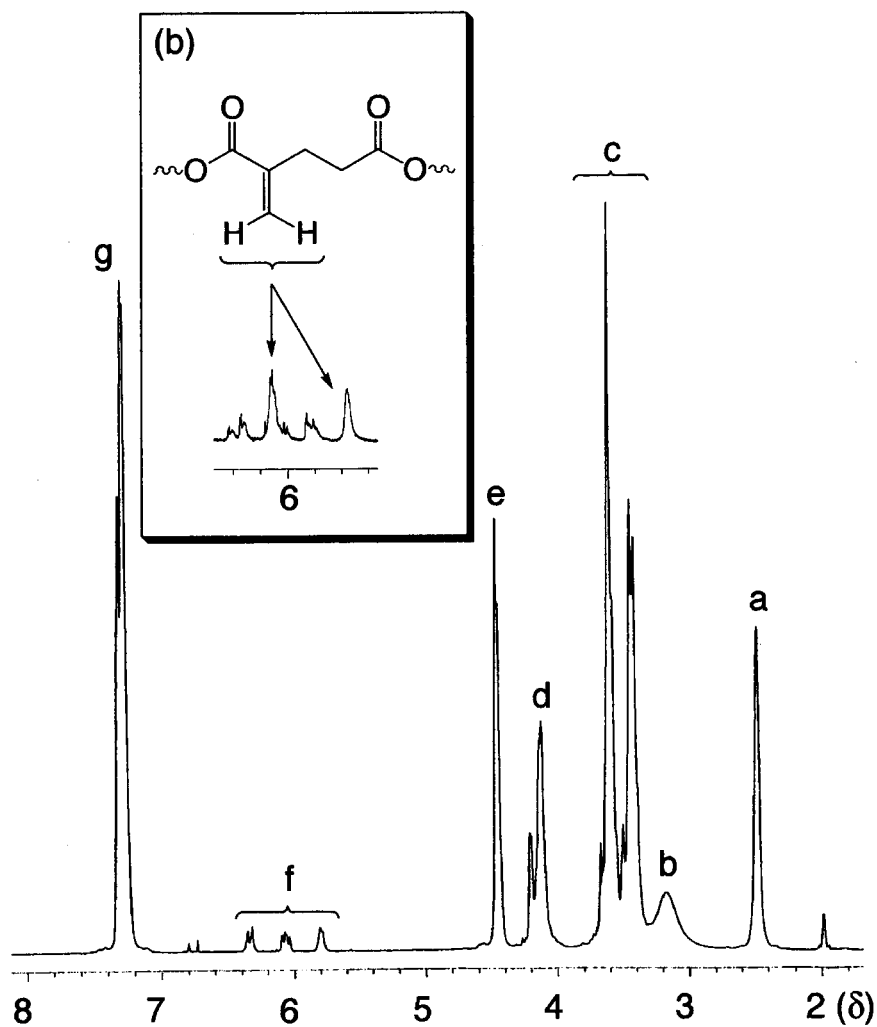
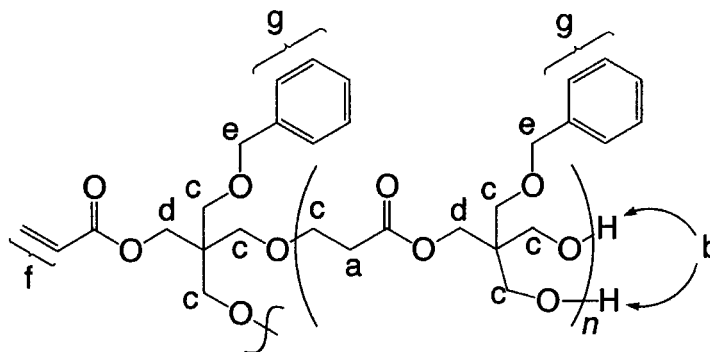*Figure 1.* ^{1}H NMR spectra of polymer **2b** obtained using sodium hydride (a) and polymer obtained using triphenylphosphine (b) in CDCl₃.
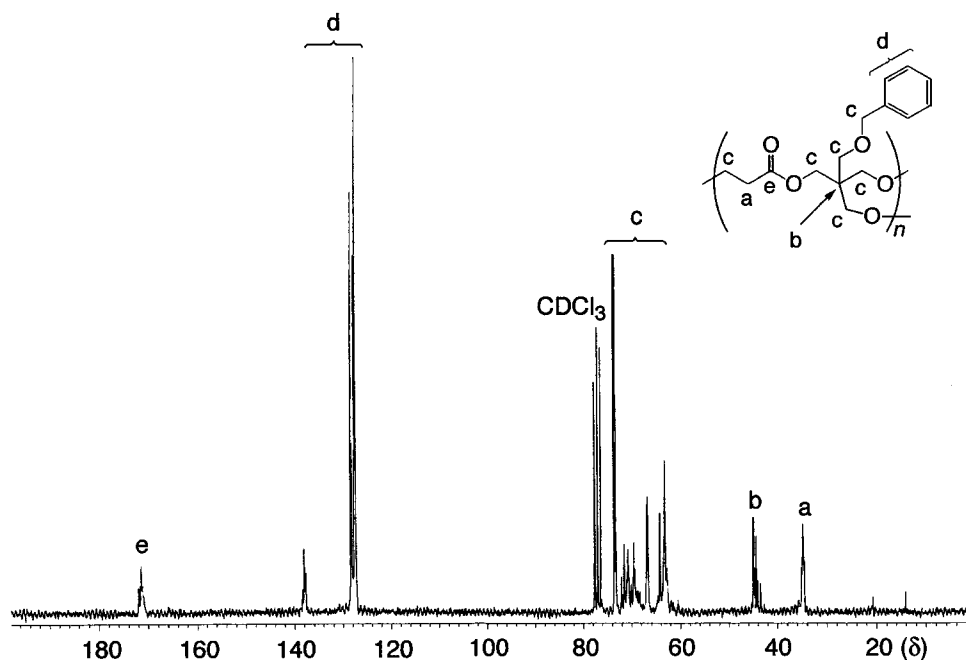
Figure 2. ^{13}C NMR spectrum of polymer **2b** in CDCl$_3$.

The degree of branching (DB) is a often used method to reveal the structure of hyperbranched polymers. The most common definition is DB = $(Br + Ter)/(Br + Li + Ter)$, where *Br* is the number of branching units, *Li* is the number of linear units, and *Ter* is the number of terminal units. The spectroscopic results of the product polymer did not offer clues to calculate DB values. For determination of the DB values, a methanolysis experiment was carried out to convert the polymers into the corresponding compounds **4**, **5**, and **6** (Sch. 3). The methanolysis products were separated by column chromatography and the ^{1}H NMR spectra of thus isolated compounds supported formation of **4**, **5**, and **6**. Furthermore, the NMR spectra showed that the peak due to OC*H*$_2$CH$_2$C=O of **5** appeared separately from other peaks. The molar ratio of **5** in the methanolysis products, therefore, could be calculated by the integrated ratio of the NMR spectrum of the methanolysis mixture, which in turn indicated the content of the linear units in the polymer. The methanolysis experiment, therefore, could be taken to determine the DB values.

Table 1 summarizes the polymerization results under the various conditions. When the amounts of sodium hydride were larger than 20% for **1b**, the polymerization proceeded smoothly to produce the polymers with the molecular weights of 2700−7600 in ca. 50−76% yields. The DB values of the polymers, determined by the methanolysis experiment, were in the range of 0.5−0.6.
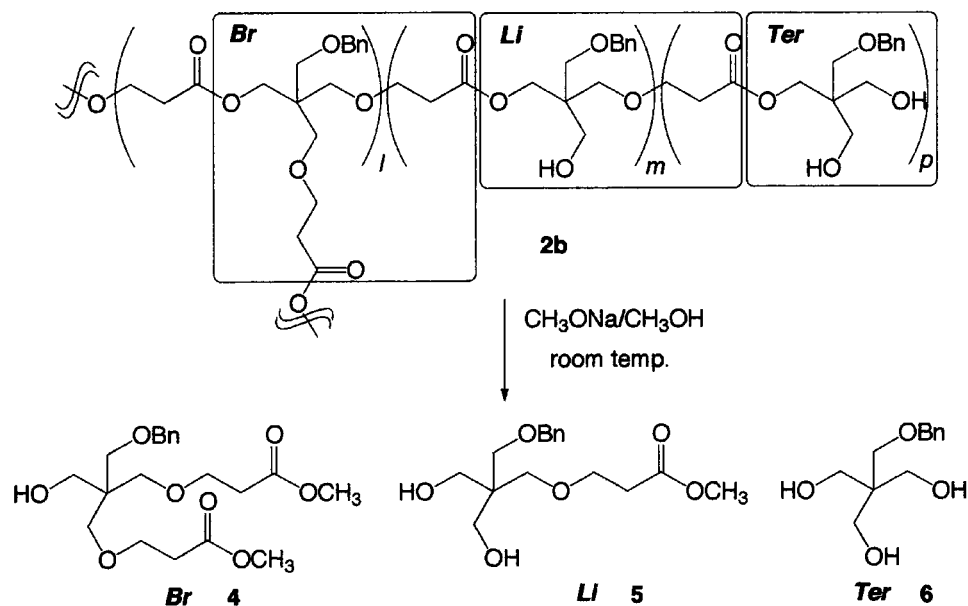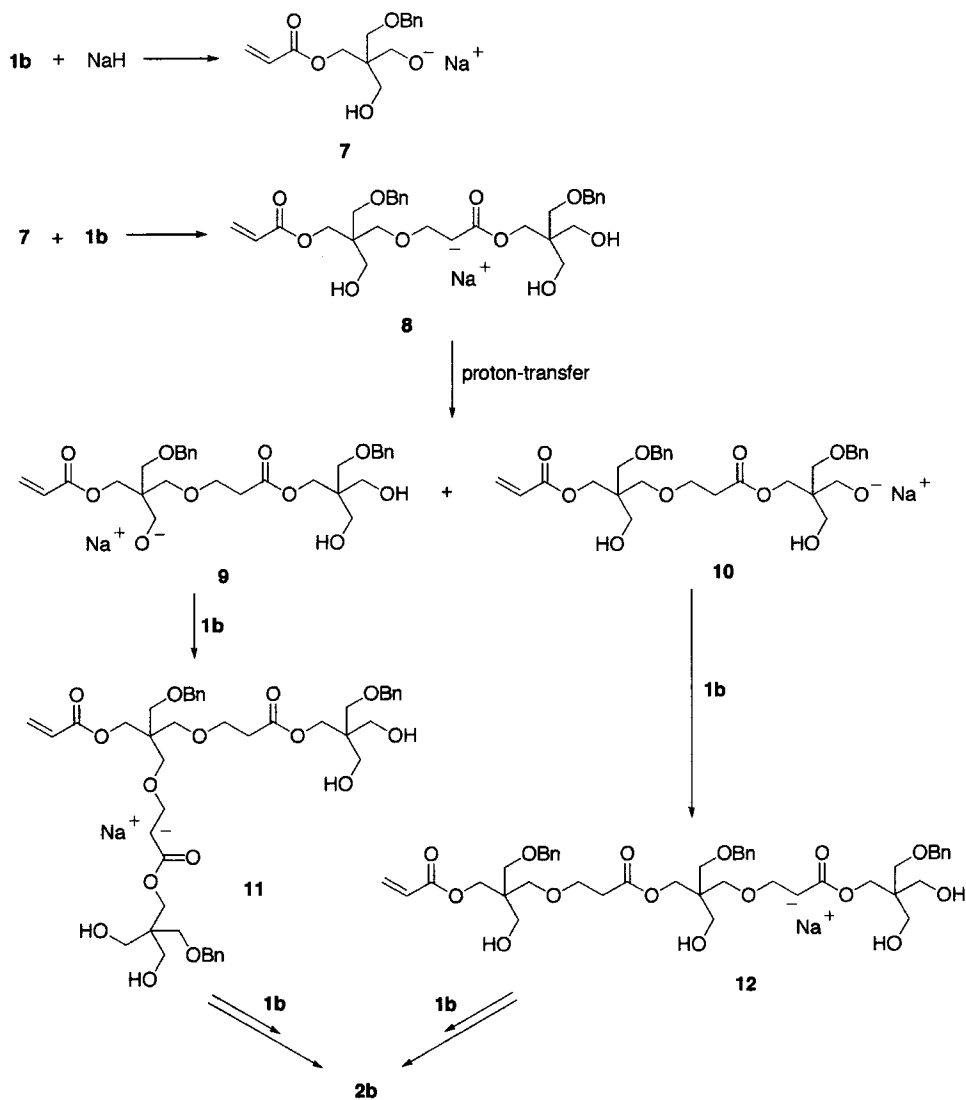
Scheme 3.

The following mechanism is proposed for the polymerization of **1b** (Sch. 4). The initiation is the formation of sodium alcoholate species **7** by the reaction of **1b** with sodium hydride. Then, the Michael-type addition of **7** onto **1b** via the proton-transfer process occurs resulting in the dimer **9** or **10**; there are two possibilities for the structures of the dimers due to the existence of two kinds of hydroxy groups in the adduct **8** from **7** and **1b**. The Michael-type addition of **9** onto **1b** produces branched species **11**, whereas the addition of **10** onto **1b** results in the linear species **12**. Then, the proton-transfer from unspecified hydroxy groups in **11** and/or **12** takes place to yield the trimers with various branched structures. The propagation proceeds via repetition of these reactions involving the frequent proton-transfer process,

Table 1. Polymerization of **1b** Initiated with Sodium Hydride Under Various Conditions

| Entry	NaH (mol%)	Temp. (°C)	Time (h)	Yield[a] (%)	M_n^b	M_w/M_n^b	DB[c]
1	30	80	24	70.1	4400	1.4	0.56
2	20	100	24	50.0	2700	1.3	0.53
3	30	100	24	75.5	3400	1.5	0.56
4	30	100	72	75.1	7600	1.5	0.57
5	40	100	24	73.9	3500	1.7	0.52

[a]Petroleum ether insoluble fraction; [b]Determined by GPC analyses with DMF as the eluent using polystyrene standards; [c]Determined by methanolysis experiments.

Scheme 4.

giving rise to the hyperbranched polymer **2b**. In the present polymerization, therefore, the hydroxy groups can be considered as the latent propagation species.

Although the monomer conversion reached quantitative under the conditions of entry 3, the molecular weight still increased by the prolonged reaction time like entry 4. This phenomenon indicates that the polymerization is probably based not only on the chain-growth mechanism as mentioned above, but also on a step-growth mechanism, in which the
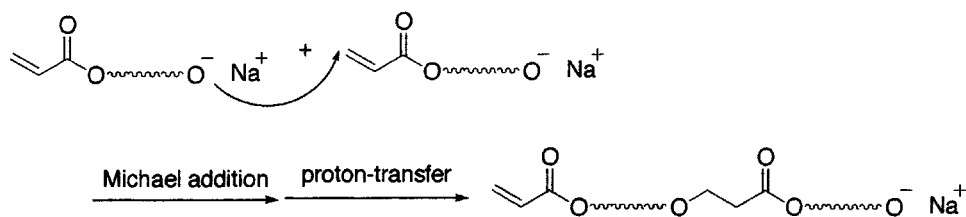
Scheme 5.

Michael-type addition of the propagating end onto the acrylate end group of the polymer probably takes place (Sch. 5).

CONCLUSION

Hyperbranched polymer was synthesized by means of the proton-transfer polymerization of an acrylate monomer **1b** containing two hydroxy groups initiated with sodium hydride. The polymerization proceeded through the Michael-type addition followed by the proton-transfer process to form the polyester-ether **2b**. The DB values were determined by the methanolysis experiment, which were the range of 0.5−0.6.

ACKNOWLEDGMENTS

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