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# Articles

## Synthesis of Hyperbranched Glycopolymers via Self-Condensing Atom Transfer Radical Copolymerization of a Sugar-Carrying Acrylate

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ABSTRACT: Hyperbranched glycopolymers were synthesized by self-condensing vinyl copolymerization (SCVCP) of an acrylic AB* inimer, 2-(2-bromopropionyloxy)ethyl acrylate (BPEA), with 3-*O*-acryloyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranoside (AIGlc) via atom transfer radical polymerization (ATRP), followed by deprotection of the isopropylidene protecting groups. Homopolymerization of AIGlc with the CuBr/pentamethyldiethylenetriamine (PMDETA) catalyst system in solution resulted in linear poly(AIGlc) having controlled molecular weights and narrow molecular weight distribution, which were characterized using GPC, GPC/viscosity, and MALDI−TOF mass spectrometry. The catalyst system could be applied for SCVCP to synthesize hyperbranched poly(AIGlc)s, in which the molecular weights, the composition of AIGlc segment, and the branched structures can be adjusted by an appropriate choice of the comonomer ratio, $\gamma$. Deprotection of the isopropylidene protecting groups of the branched poly(AIGlc)s resulted in water-soluble glycopolymers with randomly branched architectures.

## Introduction

Synthetic carbohydrate-based polymers are now being used as very important tools to investigate carbohydrate-based interactions.[1,2] Carbohydrates are involved in various biological functions in living systems. For instance, heparin, which is a natural polyanion composed of repeating dissaccharide units, is a first polysaccharide applied in medicine and plays an important role in blood coagulation.[3] Synthetic carbohydrate polymers with biocompatible and biodegradable properties are used in tissue engineering and controlled drug release devices. Many of them are used also as surfactants[4] and biologically active polymers.[5]

The new era of “glycomimics”, which are synthetic complex carbohydrates and carbohydrate-based polymers, are increasingly used for investigating glycopolymer−protein interactions.[6] These glycopolymers are widely investigated for pharmaceutical and medical applications in the treatment of infectious diseases.[7] Glycopolymers generally include natural as well as synthetic carbohydrate-bearing polymers, whereas synthetic polymers containing sugar moieties as pendant groups can be referred in a narrower sense as glycopolymers.[8] There are various types of synthetic sugar-carrying polymers. Linear polymers, comb-shaped polymers, dendrimers, and cross-linked hydrogels represent the four major classes.[9] Because of their biocompatibility and hydrophilicity, sugar-based hydrogels are used in biomedical engineering as superabsorbents, contact lenses, and matrices for drug delivery systems.[10,11]

Highly branched glycopolymers have adopted nature’s multivalent approach to their work,[12] and therefore they have been used to understand the multivalent processes. It has been reported that polyvalent saccharide ligands inhibit the protein−carbohydrate interaction, providing the best therapeutic strategy for the treatment of myriad human diseases.[13] Silylated glycodendrimers have been tested in bacterial adhesion hemagglutination assays.[14] Dendrimers with covalently attached glycoside residues in the outer layer are well-defined glycopolymer models of cell surface multiantennary glycoproteins.[15] The polyvalency inherent in carbohydrate-based polymers, especially in branched polymers, is an important feature which allows these materials to serve as cell surface mimics to understand and manipulate carbohydrate−protein interactions.

The recent developments in the field of glycoscience, glycotechnology, and the potential applications of glycopolymers have attracted researchers to develop new synthetic routes to design a variety of sugar-containing polymers with controlled architectures and functionalities. Various polymerization techniques have been developed to synthesize sugar-containing polymers with well-defined structures, which involve cationic polymerization,[16] ring-opening polymerization,[17] ring-opening metathesis polymerization,[18] and free radical polymerization.[19] Although a variety of glycopolymers has been synthesized by conventional free radical polymerization of vinyl monomers carrying sugar residues, it was difficult to control molecular weights and architecture.

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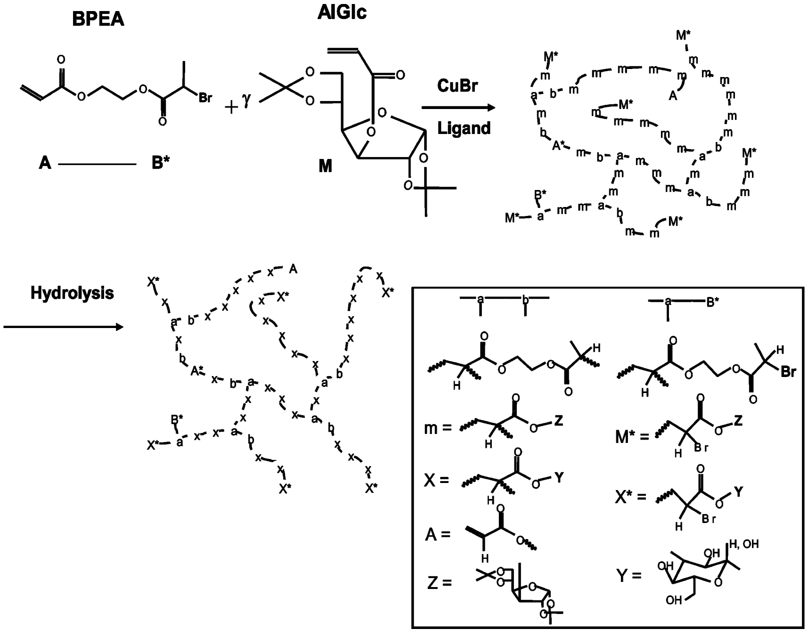
**Scheme 1. General Route to Branched Glycopolymers via Self-Condensing Vinyl Copolymerization, Followed by Deprotection of Isopropylidene Protecting Groups**



Controlled/“living” radical polymerization has allowed well-defined and controlled synthesis of glycopolymers by a very facile and simple approach. For example, Fukuda et al. have reported the synthesis of styryl and methacryloyl monomers having a saccharide residue by using nitroxide-mediated polymerization[20] and atom transfer radical polymerization (ATRP).[21] They also have reported the synthesis of glycopolymers by nitroxide-mediated polymerization of a sugar-carrying acrylate, but the system gave polymers with limited conversion.[22] Gotz et al. have reported the synthesis of new lipo-glycopolymer amphiphiles, which were prepared by nitroxide-mediated polymerization with a dioctadecyl-substituted nitroxide initiator and 1,2,5,6-di(isopropylidene)-D-glucose-2-propenoate as monomer.[23] ATRP has been used for the synthesis of many sugar-carrying block[24,25] and graft polymers.[26] Very recently, Narain and Armes reported the first ATRP of unprotected sugar-based monomers.[27,28]

This paper reports the synthesis of randomly branched glycopolymers using self-condensing vinyl copolymerization (SCVCP) of an acrylic AB* inimer, 2-(2-bromopropionyloxy)ethyl acrylate (BPEA) with 3-*O*-acryloyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranoside (AIGlc) via ATRP. The synthetic route to highly branched glycopolymers is given in Scheme 1. The curved lines represent polymer chains. A*, B*, and M* are active units, whereas a, b, and m are reacted ones. A is an acryloyl group. M and m stand for AIGlc units at the chain end and in the linear segment, respectively. SCVCP of AB* inimers with conventional monomers is a facile approach to obtain functional branched polymers because different types of functional groups can be incorporated into a polymer, depending on the chemical nature of the comonomer.[29−32] In this study, an isopropylidene-protected sugar-carrying acrylate, AIGlc, was selected as a comonomer for the synthesis of water-soluble highly branched glycopolymers. For an ideal SCVCP process, living polymerization systems are required to avoid cross-linking reactions and gelation due to chain transfer or recombination reactions. Hence, the important step is to find suitable conditions where both homoplymerization of AIGlc and homo-SCVP of the inimer can proceed in a controlled/“living” fashion. In general, Cu-based ATRP was employed for SCV(C)P of acrylate-type inimers having an acrylate (A) and a bromoester group (B*), capable to initiate ATRP.[33] In this study, we used the CuBr/pentamethyldiethylenetriamine (PMDETA) catalyst system to prepare well-defined and monodisperse linear poly(AIGlc). Effects of temperature and solvents were investigated in terms of the polydispersity and polymerization rate. Randomly branched poly(AIGlc)s having different molecular weights and degree of branching were synthesized by SCVCP with different comonomer ratios, $\gamma$, via ATRP.

## Experimental Section

**Materials**. CuBr (95%, Aldrich) was purified by stirring overnight in acetic acid. After filtration, it was washed with ethanol, ether, and then dried. *N,N,N′,N″,N″*-Pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) and ethyl 2-bromo-2-isobutyrate (98%, Aldrich) were distilled and degassed. Synthesis of an acrylic AB* inimer, 2-(2-bromopropionyloxy)ethyl acrylate (BPEA), was conducted by the reaction of 2-bromo-propinoyl bromide with 2-hydroxyethyl acrylate in the presence of pyridine as reported previously.[34,35] The inimer was degassed by three freeze−thaw cycles. Other reagents were commercially obtained and used without further purification.

**Synthesis of 3-*O*-Acryloyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranoside (AIGlc).** The synthesis of AIGlc was carried out according to the method reported by Fukuda et al.[22] and Ouchi et al.[36] with slight modifications. To a solution of 1,2:5,6-di-*O*-isopropylidene-D-glucofuranose (10 g, 38.5 mmol) in acetone (50 mL) was added a 5 N solution of NaOH (11.55 mL, 57.8 mmol), and then acryloyl chloride (3.4 mL, 38.5 mmol) was added dropwise to the mixture with stirring in an ice bath. After 1 h it was allowed to stir at room temperature for 48 h. Then the reaction mixture was diluted with 100 mL of water and extracted with *n*-hexane. The aqueous layer was washed two times with hexane, and the combined extract was washed three times with water to remove the salts. It was then dried over anhydrous sodium sulfate. The drying agent was filtered off, and the filtrate was evaporated under reduced pressure to give a crude syrup. The crude syrup was distilled under a very high vacuum (90 °C, $1 \times 10^{-2}$ mbar) to give white solid, 5.0 g (41%). $^1$H NMR (CDCl$_3$): $\delta = 1.25-1.55$ (m, 12H,

**Table 1. Homopolymerization of 3-*O*-Acryloyl-1,2:5,6-di-*O*-isopropylidene-α-D-Glucofuranoside (AIGlc) with CuBr/PMDETA at 60 °C in Ethyl Acetate (50 wt %)[a]**

| $[M]_0/[I]_0$ | time (h) | conv[b] (%) | $M_{n,\text{calcd}}$[c] | $M_{n,\text{GPC}}$[d] ($M_w/M_n$) | $M_{n,\text{GPC-VISCO}}$[e] ($M_w/M_n$) | $M_{n,\text{MALDI}}$[f] ($M_w/M_n$) |
|---|---|---|---|---|---|---|
| 15 | 18 | 73 | 3400 | 4100 (1.05) | | 3200 (1.14) |
| 20 | 48 | 88 | 5500 | 5900 (1.09) | 6600 (1.13) | 5400 (1.09) |
| 50 | 72 | 93 | 14600 | 13400 (1.09) | 18500 (1.25) | 13600 (1.11) |
| 100 | 48 | 33 | 10300 | 9300 (1.06) | 14800 (1.17) | 9400 (1.13) |
| 100 | 120 | 84 | 26300 | 24200 (1.14) | 30900 (1.37) | 29200 (1.12) |

[a] Solution polymerization with ethyl 2-bromoisobutyrate; $[I]_0:[CuBr]_0:[PMDETA]_0 = 1:1:1$. [b] Monomer conversion as determined by $^1$H NMR. [c] Theoretical number-average molecular weight as calculated from the monomer conversion. [d] Determined by GPC using THF as eluent with PtBuA standards. [e] Determined by GPC−viscosity measurement. [f] Determined by MALDI−TOF MS measurement.

isopropylidene units), 4.05, 4.25, 5.29, 5.87 (7H, sugar moiety), 5.85−6.50 (3H, three vinyl protons). $^{13}$C NMR ($CDCl_3$): $\delta$ = 165.05 ($C$=O), 131.6 ($C$H$_2$=), 128.09 ($C$H=), 27.18, 27.07, 26.56, 25.59 ($C$H$_3$ in isopropylidene groups).

**Atom Transfer Radical Polymerization of AIGlc.** All polymerizations were carried out in a round-bottom flask sealed with a plastic cap. A representative example is as follows: Ethyl 2-bromoisobutyrate (0.0254 g, 0.127 mmol) was added to a round-bottom flask containing CuBr(I) (0.0178 g, 0.127 mmol), PMDETA (0.0219 g, 0.127 mmol), and AIGlc (0.80 g, 2.54 mmol) in ethyl acetate (0.80 g, 50 wt % to AIGlc). As soon as the initiator was added to the mixture, the color changed into green, indicating the start of the polymerization. The flask was placed in an oil bath at 60 °C for 48 h. Conversion of the double bonds, as detected by $^1$H NMR, was 88%. The content in the flask was viscous which was dissolved in THF. The solution was passed through a silica column, and the polymer was precipitated from THF into hexane. Finally, the product was freeze-dried from dioxane and dried under vacuum at room temperature. The polymer had $M_n = 5900$ and $M_w/M_n = 1.09$ according to conventional GPC, $M_n = 6600$ and $M_n/M_w = 1.13$ according to GPC/visosity using universal calibration, and $M_n = 5400$ and $M_w/M_n = 1.09$ according to MALDI−TOF MS measurement.

A mixture of linear poly(AIGlc)s with various molecular weights was used as comparison in the solution viscosity studies. Molecular weight for this sample: $M_n = 13\,800$ and $M_w/M_n = 1.64$ (determined by GPC/viscosity using universal calibration) as shown in Figure S-1 (see Supporting Information).

**Self-Condensing Vinyl Copolymerization.** A representative example for the copolymerization ($\gamma = [\text{AIGlc}]_0/[\text{BPEA}]_0 = 1$) is as follows: BPEA (0.3995 g, 1.592 mmol) was added to a round-bottom flask containing CuBr(I) (0.004 78 g, 0.0318 mmol), PMDETA (0.005 49 g, 0.0318 mmol), AIGlc (0.5 g, 1.592 mmol), and ethyl acetate (0.5 g, 50 wt % to AIGlc). As soon as BPEA was added to the mixture, the color changed into green, indicating the start of the polymerization. The flask was placed in an oil bath at 60 °C for 4 h. The mixture was completely solidified after 4 h when the conversion reached a certain level. Conversion of the double bonds, as detected by $^1$H NMR, was 90%. After the mixture was dissolved in THF, and was passed through a silica column, the polymer was precipitated from THF into hexane. Then the product was freeze-dried from dioxane and finally dried under vacuum at room temperature to yield a white powder. The polymer had $M_n = 7800$ and $M_w/M_n = 1.43$ according to conventional GPC and $M_n = 9200$ and $M_w/M_n = 2.84$ according to GPC/viscosity using universal calibration. The resulting polymer was soluble in chloroform, THF, and acetone but insoluble in methanol, hexane, and water.

**Deprotection.** Transformation of randomly branched poly(AIGlc) into branched poly(3-*O*-acryloyl-α,β-D-glucopyranoside) (AGlc) was achieved under mild acidic conditions. The branched poly(AIGlc) ($\gamma = 1$; 85 mg) was dissolved in 80% formic acid (10 mL) and stirred for 48 h at room temperature. Then, 4 mL of water was added, and it was stirred for another 3 h. The solution was dialyzed using Spectra/Por$^R$ (MWCO: 1000) against Millipore water for 2 days. The solution was evaporated under reduced pressure, and the resulting polymer was freeze-dried from dioxane and dried under vacuum. The deprotected hyperbranched polymer ($\gamma = 1$) was obtained as white powder in a quantitative yield (75 mg, yield = 88%), which was insoluble in water, methanol, and acetone and completely soluble in DMSO. The deprotection was done in a similar way in the case of linear poly(AIGlc), which gave water-soluble glycopolymers.

**Characterization.** The linear and branched polymers obtained from AIGlc were characterized by conventional GPC and GPC/viscosity using THF as eluent at a flow rate of 1.0 mL/min at room temperature. A conventional THF-phase GPC system was used to obtain apparent molecular weights. GPC system I; column set: 5 μm PSS SDV gel, $10^2$, $10^3$, $10^4$, $10^5$ Å, 30 cm each; detectors: Waters 410 differential refractometer and Waters photodiode array detector operated at 254 nm. Narrow PtBuA standards (PSS, Mainz) were used for the calibration of the column set I. Molecular weights of the branched polymers were determined by the universal calibration principle[37] using the viscosity module of the PSS−WinGPC scientific V 6.1 software package. Linear PMMA standards (PSS, Mainz) were used to construct the universal calibration curve. GPC system II; column set: 5 μm PSS SDV gel, $10^3$ Å, $10^5$ Å and $10^6$ Å, 30 cm each; detectors: Shodex RI-71 refractive index detector; Jasco Uvidec-100-III UV detector ($\lambda = 254$ nm); Viscotek viscosity detector H 502B. A 1-methyl-2-pyrrolidone (NMP)-phase GPC system was used to obtain apparent molecular weights of the hydrolyzed polymers. GPC system III; column set: two PSS GRAM 7 μm, 1000 and 100 Å columns thermostated at 70 °C; detectors: Waters 486 UV detector ($\lambda = 270$ nm), and Bischoff RI-detector 8110. 50 μL of the sample diluted in NMP (containing 0.05 M LiBr) were injected at a flow rate of 1 mL/min. Linear PS standards were used for calibration.

MALDI−TOF mass spectrometry was performed on a Bruker Reflex III instrument equipped with a 337 nm $N_2$ laser in the reflector mode and 20 kV acceleration voltage. 2,5-Dihydroxybenzoic acid (Aldrich, 97%) was used as a matrix. Samples were prepared from THF solution by mixing matrix (20 mg/mL) and polymer (10 mg/mL) in a ratio of 4:1. The number-average molecular weights of the polymers were determined in the linear mode.

$^1$H and $^{13}$C NMR spectra were recorded with a Bruker AC-250. FT-IR spectra were recorded on a Bruker Equinox 55 spectrometer. The elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium (Kulmbach).

## Results and Discussion

**Effect of Polymerization Conditions on the Homopolymerization of AIGlc.** To find the suitable polymerization conditions for the synthesis of highly branched glycopolymers by SCVCP, we first investigated the effect of polymerization conditions on ATRP of AIGlc. In a previous paper, we have demonstrated that the synthesis of randomly branched polymers by SCVCP of *tert*-butyl acrylate with BPEA was achieved using CuBr/PMDETA catalyst system.[38] Hence, the CuBr/PMDETA catalyst system was employed for ATRP of AIGlc. When AIGlc was polymerized using CuBr/PMDETA with ethyl 2-bromoisobutyrate ($[M]_0/[I]_0 = 20$) at 60 °C in ethyl acetate, as shown in Table 1, the conversion reached 88% (as determined by $^1$H NMR)

**Table 2. Effects of Solvent and Temperature on Homopolymerization of AIGlc with CuBr/PMDETA**

| solvent[a] | temp (°C) | $[M]_0/[I]_0$ | time (h) | conv[b] (%) | $M_{n,calcd}$ | $M_{n,GPC}$[c] ($M_w/M_n$) |
|---|---|---|---|---|---|---|
| ethyl acetate | 60 | 50 | 72 | 93 | 14600 | 13400 (1.09) |
| ethyl acetate | 60 | 100 | 48 | 33 | 10300 | 9300 (1.06) |
| ethyl acetate | 80 | 50 | 48 | 77 | 12800 | 14900 (1.27) |
| ethyl acetate | 80 | 100 | 24 | 47 | 14700 | 13500 (1.18) |
| anisole | 80 | 50 | 24 | 93 | 15700 | 14700 (1.25) |
| anisole | 100 | 100 | 24 | 79 | 23100 | 24800 (1.26) |

[a] 50 wt %; $[I]_0$:$[CuBr]_0$:$[PMDETA]_0$ = 1:1:1. [b] Monomer conversion as determined by $^1$H NMR. [c] Determined by GPC using THF as eluent with PtBuA standards.

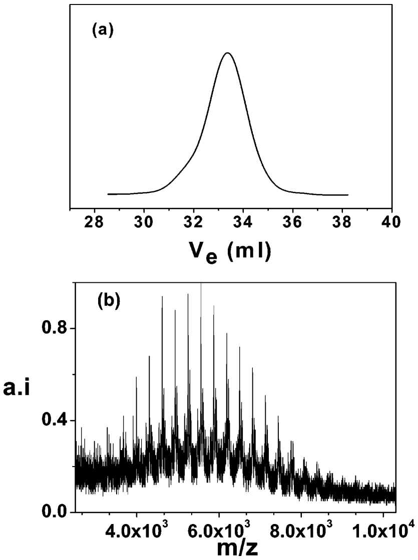


**Figure 1.** (a) GPC trace (RI signal) and (b) MALDI−TOF mass spectrum (linear mode) of linear poly(AIGlc) obtained by CuBr/PMDETA at $[M]_0/[I]_0$ = 20. See Table 1 for detailed polymerization conditions.

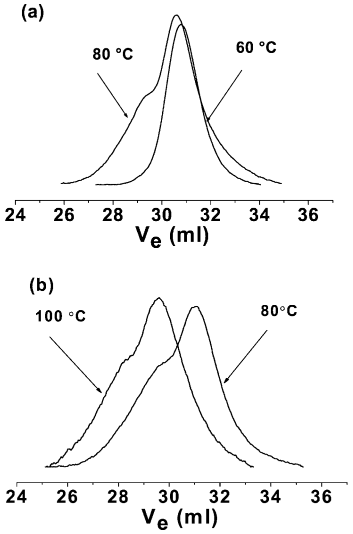


**Figure 2.** GPC traces of linear poly(AIGlc) (a) in ethyl acetate at 60 and 80 °C ($[M]_0/[I]_0$ = 50) and (b) in anisole at 80 °C ($[M]_0/[I]_0$ = 50) and 100 °C ($[M]_0/[I]_0$ = 100). See Table 2 for polymerization conditions.

after 48 h. The number-average molecular weight of poly(AIGlc) as determined by conventional GPC using PtBuA standards was $M_n = 5900$, which is almost the same as the theoretical value ($M_n = 5500$), and the polydispersity index was $M_w/M_n = 1.09$. As can be seen later, the linear and branched polymers obtained from AIGlc were evaluated by conventional GPC and GPC/viscosity systems, as the relation between molecular weight and hydrodynamic volume of branched polymers differs substantially from the linear ones. In addition, the bulky side group in poly(AIGlc) may lead to different hydrodynamic volume compared to that of standard PtBuA. To clarify these points, further characterization was conducted using GPC/viscosity and MALDI−TOF mass spectrometry (MS). As can be seen in Figure 1, the molecular weights and molecular weight distributions obtained from MALDI−TOF MS ($M_n = 5400$ and $M_w/M_n = 1.09$) and GPC/viscosity ($M_n = 6600$ and $M_w/M_n = 1.09$) are in agreement with those obtained from the conventional GPC using PtBuA standards and with the theoretical values.

Table 1 shows the results of homopolymerization obtained at different monomer-to-initiator ratios, $[M]_0/[I]_0$. For the cases of the polymerization at $[M]_0/[I]_0 = 100$, a longer polymerization time was required to attain higher conversion (conversion = 84% for 120 h and 33% for 48 h). The polymerization mixture was still liquid after 48 h, but it became viscous and the polymerization was stopped after 120 h, whereas almost full conversion was obtained after 72 h in the case of $[M]_0/[I]_0 = 50$. As can be seen in Table 1, the polymerization in ethyl acetate using the CuBr/PMDETA system gave linear poly(AIGlc)s with low narrow polydispersity ($1.05 < M_w/M_n < 1.14$) with predicted molecular weights in the range of $[M]_0/[I]_0 = 20−100$. These results suggest that the CuBr/PMDETA catalyst at 60 °C is a suitable system for the controlled polymerization of AIGlc. In all cases, the expected molecular weights and narrow molecular weight distributions could be achieved regardless of $[M]_0/[I]_0$, suggesting that the extremely slow polymerization compared to other type of acrylates is simply due to the steric hindrance by the bulky side group in the sugar-carrying acrylate. A similar tendency was also observed in the nitroxide-mediated polymerization of AIGlc, which resulted in limited conversion (~55%) and molecular weights ($M_n = {\sim}13\,000$) with relatively low polydispersity ($1.2 < M_w/M_n < 1.6$).[22] On the other hand, our ATRP system provided polymers with almost full conversion having higher molecular weights ($M_n > 2 \times 10^4$) and narrower molecular weight distributions ($M_w/M_n < 1.14$).

The homopolymerization of AIGlc was conducted under various conditions, aiming at increasing the polymerization rate as well as understanding the effects of solvent and temperature. The results are summarized in Table 2. The polymerization in ethyl acetate at 80 °C led to increase of the reaction rate but gave a bimodal distribution curve, as shown in Figure 2a. Note that the polymerization at higher concentration (with less solvent) is also not suitable because the solubility of the monomer is not so high; the solubilization process is slow even in ethyl acetate (50 wt % to AIGlc) and takes a prolonged time to dissolve completely. The polymerization in anisole at 80 and 100 °C also gave polymers having bimodal distribution (Figure 2b). This could be

**Table 3. Self-Condensing Vinyl Copolymerization of BPEA and AIGlc under Various Conditions**[a]

| solvent[b] | temp (°C) | time (h) | conv[c] (%) | $M_{n,GPC}$[d] ($M_w/M_n$) | $M_{n,GPC-viscosity}$[e] ($M_w/M_n$) | α[f] | DB[g] |
|---|---|---|---|---|---|---|---|
| ethyl acetate | 60 | 4 | 48 | 3100 (1.54) | 4800 (1.78) | 0.19 | 0.39 |
| ethyl acetate | 60 | 24 | 98 | 5180 (1.79) | 6600 (1.92) | 0.24 | 0.42 |
| ethyl acetate | 80 | 24 | 95 | 4800 (1.60) | 5300 (2.21) | 0.23 | 0.42 |
| anisole | 80 | 24 | 58 | 2900 (1.43) | 4400 (1.68) | 0.08 | 0.41 |

[a] Copolymerization at a constant comonomer ratio, $\gamma = [\text{AIGlc}]_0/[\text{BPEA}]_0 = 1.5$, and a constant comonomer-to-catalyst ratio, $\mu = ([\text{AIGlc}]_0 + [\text{BPEA}]_0)/[\text{CuBr}]_0 = 100$. [b] Ethyl acetate or anisole (50 wt % to AIGlc) was used as a solvent. [c] Conversion of double bonds as determined by $^1$H NMR. [d] Determined by GPC using THF as eluent with PtBuA standards. [e] Determined by GPC/viscosity measurement. [f] Mark–Houwink exponent as determined by GPC/viscosity measurement. [g] Degree of branching as determined by $^1$H NMR using eq 2, before hydrolysis.

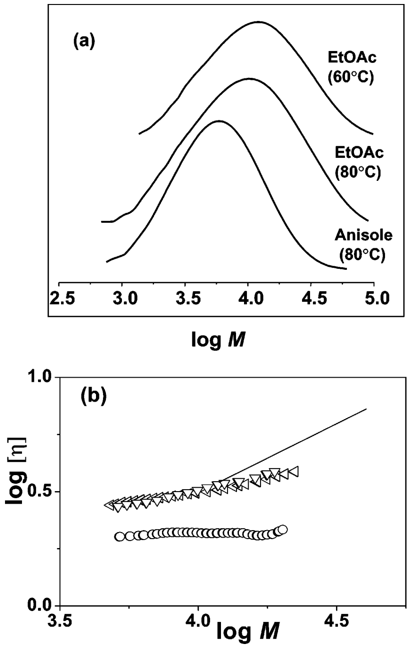


**Figure 3.** RI signals (a) and Mark–Houwink plots (b) for the polymers obtained by copolymerizations of BPEA and AIGlc at a constant comonomer ratio, $\gamma = [\text{AIGlc}]_0/[\text{BPEA}]_0 = 1.5$ in anisole at 80 °C (○), in ethyl acetate (EtOAc) at 80 °C (tilted ▽), and in ethyl acetate (EtOAc) at 60 °C (▽). The intrinsic viscosity of linear poly(AIGlc) (—) is given for comparison. See Table 3 for detailed polymerization conditions.

due to recombination occurring at higher temperatures. These results suggest that the CuBr/PMDETA system at 60 °C in ethyl acetate (50 wt % to AIGlc) is a suitable system for controlled polymerization of AIGlc, but the increase of the polymerization temperature may lead to unfavorable side reactions.

**Effect of Polymerization Conditions on SCVCP of BPEA with AIGlc.** Copolymerizations were conducted with CuBr/PMDETA in ethyl acetate at a constant comonomer-to-catalyst ratio, $\mu = ([\text{AIGlc}]_0 + [\text{BPEA}]_0)/[\text{CuBr}]_0 = 100$, and a constant comonomer ratio, $\gamma = [\text{AIGlc}]_0/[\text{BPEA}]_0 = 1.5$. The results are summarized in Table 3. The comparisons of the Mark–Houwink plots are given in Figure 3.

When the SCVCP of AIGlc with BPEA was carried out in ethyl acetate at 60 °C, 48% conversion was reached after 4 h. Almost full conversion was reached only after 24 h, owing to the slow rate of polymerization of AIGlc as discussed earlier. As can be seen from Table 3, $M_{n,\,GPC-VISCO} = 6600$ and $M_w/M_n = 1.92$ were obtained at almost full conversion. When the reaction was conducted in ethyl acetate at 80 °C after 24 h, the results are comparable to those obtained at 60 °C. In both cases, the Mark–Houwink exponents of the branched polymers in THF (α = 0.23–0.24) are significantly lower than that for linear poly(AIGlc) (α = 0.52 ± 0.03). As can be seen in Figure 3b, the absolute intrinsic viscosities of the branched polymers are significantly lower than those of the linear one in the higher molecular weight range ($M > 10^4$), suggesting a more compact architecture with lower intrinsic viscosity. Note that the viscosity values of the linear polymers are comparable to those of the branched polymers in the low molecular weights range ($M < 10^4$), suggesting that the macroscopic quantities such as intrinsic viscosity and radius of gyration of linear polymers are more or less similar to those of branched ones due to the bulky side groups. However, in the higher molecular weight range, the influence of the bulky side groups is less significant, and the branched structures leads to compact architectures and a decrease in the viscosity. In other words, the bulky side group has significant influence not only on the polymerization rate but also on the solution behavior in low molecular weight area. When the same polymerization was carried out in anisole at 80 °C, the reaction mixture turned brown after 24 h, and there was an apparent lowering of molecular weights ($M_{n,GPC-VISCO} = 4400$ and $M_w/M_n = 1.68$) with lower conversion (58% even after 24 h). The α value was around 0.08, which is significantly less than that of typical hyperbranched polymers. Moreover, the homopolymerization at 80 °C gave a bimodal GPC curve, as discussed in the previous section. Hence, SCVCP of AIGlc and BPEA with CuBr/PMDETA in ethyl acetate using at 60 °C was selected for our further investigations toward the synthesis of highly branched glycopolymers.

**Effect of the Comonomer Ratio on the SCVCP of BPEA with AIGlc.** The effect of the comonomer ratio on SCVCP of BPEA with AIGlc was investigated with the CuBr/PMDETA system in ethyl acetate. The copolymerization was carried out at 60 °C at different comonomer ratios, $\gamma = [\text{AIGlc}]_0/[\text{BPEA}]_0$ between 1 and 10, keeping the comonomer-to-catalyst ratio at a constant value of $\mu = ([\text{AIGlc}]_0 + [\text{BPEA}]_0)/[\text{CuBr}]_0 = 100$. In the case of $\gamma = 1$, almost 90% conversion was achieved after 4 h. However, in the case of $\gamma = 1.5$ the conversion was 48% even after 4 h. Hence, the polymerization time was adjusted, depending on the comonomer ratio, $\gamma$, because the achievement of almost full conversion is one of important factors to obtain higher molecular weights and degree of branching.[30] Actually, the time was prolonged until the reaction mixture became viscous. For $\gamma$ values ranging from 2.5 to 10, almost full conversion was achieved after 24–120 h, as shown in Table 4. The molecular weights and molecular weight distribution of the copolymers were characterized by GPC/viscosity using universal calibration and conventional GPC. In all cases, the molecular weights determined by GPC/viscosity are higher than the apparent ones obtained by GPC, indicating highly branched structures.

**Table 4. Self-Condensing Vinyl Copolymerization of BPEA and AIGlc at Different Comonomer Ratios $\gamma^a$**

| | | | | | | BPEA ratio in polymer | | |
|---|---|---|---|---|---|---|---|---|
| $\gamma^b$ | time (h) | conv$^c$ (%) | $M_{n,GPC}{}^d$ ($M_w/M_n$) | $M_{n,GPC-viscosity}{}^e$ ($M_w/M_n$) | $\alpha^f$ | calcd$^g$ | obsd (NMR)$^h$ | obsd (EA)$^i$ |
| 1 | 4 | 90 | 7800 (1.43) | 9200 (2.84) | 0.20 | 0.50 | 0.41 | 0.49 |
| 1.5 | 24 | 98 | 5200 (1.79) | 6600 (1.92) | 0.24 | 0.40 | 0.39 | 0.46 |
| 2.5 | 24 | 91 | 4900 (1.49) | 5100 (2.13) | 0.24 | 0.28 | 0.33 | 0.29 |
| 5 | 72 | 95 | 5500 (1.48) | 11900 (1.59) | 0.27 | 0.16 | 0.19 | 0.17 |
| 10 | 120 | 96 | 5400 (1.37) | 13000 (1.95) | 0.28 | 0.09 | 0.08 | 0.10 |

[a] Copolymerization at 60 °C with CuBr/PMDETA at a constant comonomer-to-catalyst ratio, $\mu = ([\text{AIGlc}]_0 + [\text{BPEA})_0])/[\text{catalyst}]_0) = 100$ in the presence of ethyl acetate (50 wt % to AIGlc). [b] $\gamma = [\text{AIGlc}]_0/[\text{BPEA}]_0$. [c] Conversion of double bonds as determined by $^1$H NMR. [d] Determined by GPC using THF as eluent with PtBuA standards. [e] Determined by GPC/viscosity measurement. [f] Mark−Houwink exponent as determined by GPC/viscosity measurement. [g] Calculated from the composition in feed. [h] Determined by $^1$H NMR. [i] Determined from elemental analysis using the bromine content.

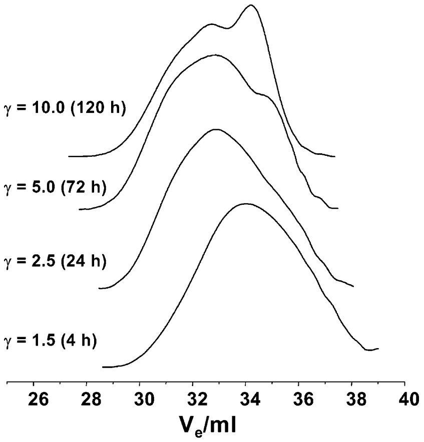


**Figure 4.** GPC traces of branched copolymers obtained by SCVCP of BPEA and AIGlc at different comonomer ratios, $\gamma = [\text{AIGlc}]_0/[\text{BPEA}]_0$. See Table 3 for $\gamma = 1.5$ (4 h) and Table 4 for $\gamma = 2.5$, 5, and 10 for detailed polymerization conditions.

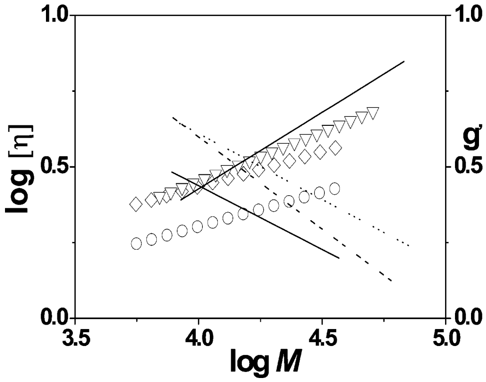


**Figure 5.** Mark−Houwink plots for the polymers obtained by copolymerizations of BPEA and AIGlc: $\gamma = 1$ (○), 2.5 (◇), 5 (▽). The intrinsic viscosity of a linear poly(AIGlc) (—) is given for comparison. Contraction factors, $g' = [\eta]_{\text{branched}}/[\eta]_{\text{linear}}$, for the polymers obtained by SCVCP of BPEA and AIGlc: $\gamma = 1$ (—), 2.5 (- -), 5.0 (···). See Table 4 for detailed polymerization conditions.

As can be seen in Figure 4, the elution curves shift toward higher molecular weights with increasing comonomer ratio, $\gamma$. In general, the number-average molecular weights of branched polymers obtained by SCVCP increase with $\gamma$, and such a tendency was observed in the SCVCP of *tert*-butyl acrylate with BPEA[38] as well as in the solution polymerization of 2-(diethylamino)-ethyl methacrylate with a methacrylate-type inimer.[31] In this study, molecular weights up to $M_{n,GPC-VISCO} = 13\,000$ could be obtained at $\gamma = 10$, whereas the polymers obtained at lower $\gamma$ values ($\gamma = 1.5$, 2.5) had lower molecular weights, which are in accordance with the general tendency. A slight deviation from the tendency (for example, when $\gamma = 1.5$, 2.5, and 5, $M_{n,GPC-VISCO} = 6600$, 5100, and 11 900, respectively) may be related to the difference in the conversion observed at each $\gamma$ value. According to theory[29] (assuming equal reactivity of active centers), the number-average degree of polymerization increases drastically with conversion of the comonomer, especially at the end of the polymerization. We believe that the relationship between the molecular weights and $\gamma$ is independent of the polymerization and catalyst systems and may be attributed to an inherent tendency for the cyclization process in SCVCP. The SCVCP at $\gamma > 10$ is considered to be possible, but a prolonged reaction time or higher catalyst concentration is required to attain higher conversion in the cases of higher $\gamma$. This is an inherent character of the system used in this study, which is basically due to the nature of the bulky sugar-carrying acrylate. It must be noted that multimodal GPC traces obtained with $\gamma = 5$ and 10 (Figure 4) indicate the presence of fractions with different hydrodynamic volumes. The Mark−Houwink plot (Figure 5) of the corresponding polymer, however, is not affected, indicating that the different fractions have similar branched structure.

Mark−Houwink plots and contraction factors,[39] $g' = [\eta]_{\text{branched}}/[\eta]_{\text{linear}}$, as a function of the molecular weight for representative branched polymers obtained by SCVCP are shown in Figure 5. Relationships between dilute solution viscosity and molecular weight have been determined, and the Mark−Houwink constant typically varies between 0.28 and 0.2, depending on the degree of branching. In contrast, the exponent is typically in the region of 0.6−0.8 for linear homopolymers in a good solvent with a random coil conformation. The Mark−Houwink exponent of the mixture of linear poly(AIGlc)s ($\alpha = 0.52 \pm 0.03$) is lower than that of poly(*tert*-butyl acrylate) ($\alpha = 0.80$), indicating less favorable interaction with the solvent. In both cases, the exponent values are well within the range of linear homopolymers. The contraction factor is another way of expressing the compact structure of a branched polymer. From Figure 5, it is obvious that the viscosities of branched poly(AIGlc)s are significantly lower than those of the linear one and increase with $\gamma$. There were only slight differences in the slopes between the branched copolymers, but the values at each molecular weight increase with increasing $\gamma$ value. The contraction factors for all the branched copolymers decrease with increasing molecular weights. These observations indicate that the differences in the molecular weights obtained from the GPC/viscosity compared to conventional GPC arises from a systematic decrease in Mark−Houwink exponent, $\alpha$, and the contraction factor, $g'$, due to a compact

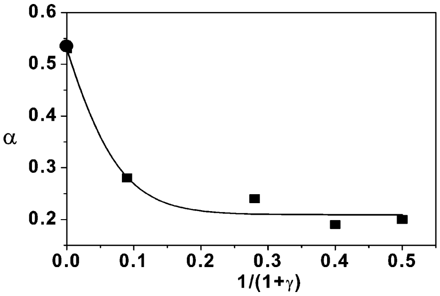


**Figure 6.** Dependence of the Mark–Houwink exponent, α, on comonomer ratio, $\gamma$ (■). (●) Linear poly(AIGlc).

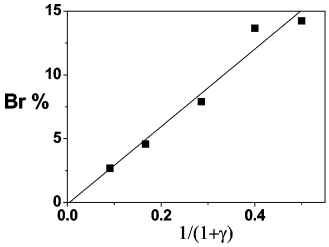


**Figure 7.** Dependence of bromine contents on $1/(\gamma + 1)$. Samples: see Table 4. The calculated value (—) is given for comparison.

structure resulting polymer from the increased number of branches.

The effect of the comonomer ratio, $\gamma$, on the Mark–Houwink exponent is shown in Figure 6. In the whole range of $\gamma$ values, the exponents of the branched polymers are significantly lower ($\alpha = 0.20-0.28$) compared to that for linear poly(AIGlc) ($\alpha = 0.52 \pm 0.03$). Such a decrease in the Mark–Houwink exponent, α, as well as the contraction factor, $g'$, provides conclusive evidence for a more compact architecture with increasing number of branches and confirms our earlier observations in SCVCP of other (meth)acrylates.[30,31]

With ATRP, nearly every chain should contain a halogen atom at its end group, if termination and transfer are essentially absent. In other words, the existence of a halogen atom at the chain end can be used as an indicator to confirm that the polymerization proceeds in controlled fashion without termination and transfer reactions. The halogen atom can be also replaced through a variety of reactions leading to end-functional polymers and used as the initiating part for polymerization of a second monomer. In the case of ideal SCVCP via ATRP, the resulting branched polymers carry one bromoester function per inimer unit, and the functionality decreases with comonomer (AIGlc) composition. As shown in Figure 7, the bromine contents of the branched polymers are dependent upon the comonomer composition in the feed and are in fair agreement with the calculated values. This result indicates the existence of reasonable number of bromine atoms at the chain ends, suggesting that unfavorable termination and transfer reactions are essentially negligible under the condition used in this study, and the number of bromoester end groups can be simply determined by the comonomer ratio, $\gamma$, in the feed.

The structure of the linear and branched poly(AIGlc)s was also confirmed by $^1$H NMR and elemental analysis. Figure 8 shows the respective $^1$H NMR spectra of the poly(AIGlc)s obtained by ATRP and SCVCP. The characteristic peaks at 1.2–1.4 (isopropylidene protons), 3.9–4.6, and 5.0–5.3 ppm are clearly seen in the linear poly(AIGlc). In the case of the copolymers, besides the signal of poly(AIGlc) segment, the BPEA inimer signals appear at 4.0–4.5 ppm attributed to the protons of the ethylene linkage and the protons which are geminal to bromine in either A*, B*, or M*, all which are derived from BPEA. The latter protons correspond to the end groups. Apart from the peak, a large doublet at 1.85 ppm in the copolymers is assigned to $CH_3$ of the 2-bromopropionyloxy group, B*, while the peak around 1.1–1.3 ppm is assigned to b, which is formed by addition of the monomer to B*. This peak b is overlapping with the isopropylidene protons of the poly(AIGlc) segment. The BPEA content in the copolymers obtained by SCVCP was determined from the $^1$H NMR spectra by comparing the peaks at 3.9–4.6 ppm attributed to the sum of five protons (A, B, C, G) of the poly(AIGlc) segment and five protons of the ethylene linkage and that geminal to bromine as mentioned above and the peak at 5.0–5.3 ppm corresponding to one proton (F) of the poly(AIGlc) segment, as shown in Figure 8. Thus, the comonomer composition can be calculated using eq 1

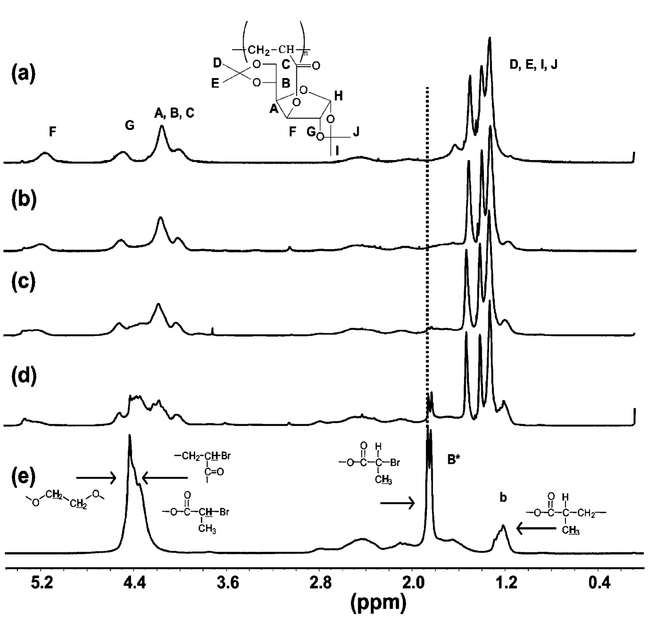


**Figure 8.** $^1$H NMR spectra ($CDCl_3$) of the linear (a) and branched poly(AIGlc): $\gamma = 5$ (b), 2.5 (c), 1 (d), and poly(BPEA) (e).[38]

$$\frac{5\mathrm{H}(x) + 5\mathrm{H}(1 - x)}{1\mathrm{H}(x)} = \frac{\text{integral at 3.9–4.6 ppm}}{\text{integral at 5.0–5.3 ppm}} \qquad (1)$$

where "$x$" is the fraction of the monomer, whereas "$1 - x$" is the fraction of the inimer in the polymer. The comonomer fractions calculated from the ratio of these peaks are in good agreement with the comonomer composition in the feed, which corresponds to the $\gamma$ value, as can be seen in Table 4. The comonomer fractions were also determined by elemental analysis via bromine content, which are also consistent with the theoretical values within experimental error. The agreements suggest complete inimer incorporation.

**Degree of Branching (DB).** Figure 8 shows $^1$H NMR spectra with the complete assignment of the linear and branched poly(AIGlc)s as well as poly(BPEA) obtained by a homo-SCVP of BPEA. For poly(BPEA), the proportions of b and B* can be calculated from the broad peak at 1.0–1.3 ppm assigned to b and large doublet at

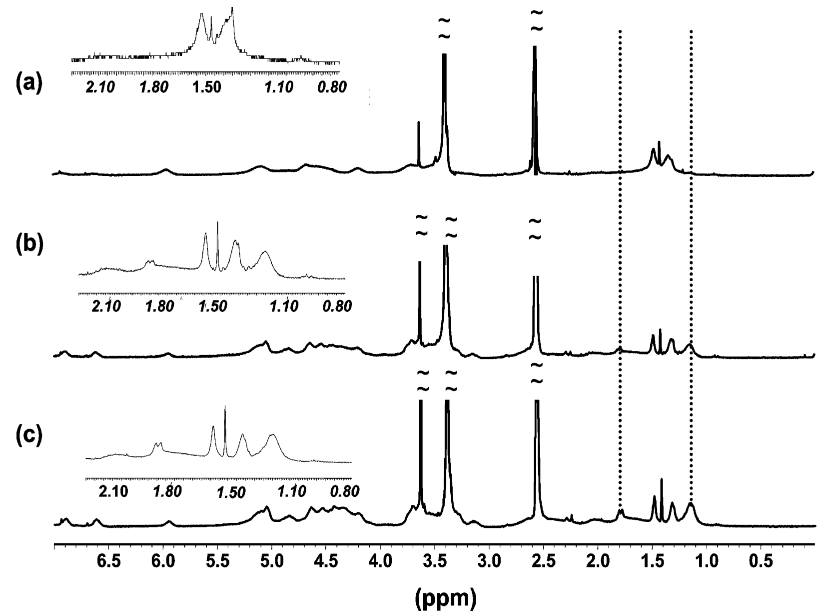


**Figure 9.** $^1$H NMR spectra (DMSO-$d_6$) of the polymers obtained after deprotection of linear poly(AIGlc) (a) and branched poly(AIGlc)s: $\gamma = 2.5$ (b), 1.5 (c).

1.85 ppm assigned to B*. In the cases of the copolymers obtained by SCVCP, these peaks should be related to the degree of branching and the comonomer composition. In our copolymerization system, since the protons of the isopropylidene groups overlap with the b protons, we have indirectly calculated the proportion of b using $^1$H NMR. For equal reactivity of active sites, the degree of branching determined by NMR, DB$_{\text{NMR}}$, at full conversion is given as[29]

$$\mathrm{DB}_{\mathrm{NMR}} = 2\left(\frac{b}{\gamma + 1}\right)\left[1 - \left(\frac{b}{\gamma + 1}\right)\right] \tag{2}$$

According to the theory of SCVCP, DB$_{\text{theo}}$, at full conversion, can be represented as

$$\mathrm{DB}_{\mathrm{theo}} = \frac{2(1 - \mathrm{e}^{-(\gamma+1)})(\gamma + \mathrm{e}^{-(\gamma+1)})}{(\gamma + 1)^2} \tag{3}$$

The fraction of b units could be calculated by comparing the peaks at 3.6−4.5 ppm and the large doublet at 1.85 ppm in the copolymers ranging from $\gamma = 1$ to 2.5. The peaks at 3.6−4.5 ppm correspond to five protons of poly(AIGlc) segment and five protons of the inimer, as mentioned earlier. The doublet at 1.85 ppm corresponds to three protons of the methyl group of B* (2-bromopropionyloxy group). Taking into account the inimer (BPEA) composition in the copolymer (see eq 1), we can calculate the integral of the peak at 1.85 ppm, corresponding to $B^*$. On the other hand, the actual ratio of the peaks at 1.85 and 3.6−4.5 ppm determined by $^1$H NMR provide the value of $B^* - b$. From these approaches, DB$_{\text{NMR}}$ = 0.43 and DB$_{\text{theo}}$ = 0.49 can be obtained at $\gamma = 1$ ($b$ = 0.65). The reliability of the method for the evaluation of b was verified by comparing the value of b after the hydrolysis of the branched and homo poly(AIGlc)s. After the hydrolysis, the isopropylidene groups disappear, and the broad peak around 1.0−1.3 ppm is clearly visible (Figure 9), which is then compared with the $B^*$ protons for the evaluation of the proportion of $b$ using the equation $b$ = (region at 1.1−1.3 ppm)/(sum of region at 1.85 ppm ($B^*$) and region at 1.1−1.3 ppm ($b$)). The values of $b$ obtained after the hydrolysis are in good agreement with the values of $b$ obtained by the indirect method, as can be seen in Table 5.

**Table 5. Degree of Branching of Copolymers Obtained by SCVCP of AIGlc and BPEA at Different Comonomer Ratios $\gamma$**

| $\gamma^a$ | $b^b$ | $b^c$ | DB$^d$ | DB$^e$ | DB$_{\text{theo}}$$^f$ |
|---|---|---|---|---|---|
| 1.0 | 0.65 | 0.60 | 0.43 | 0.42 | 0.49 |
| 1.5 | 0.75 | 0.67 | 0.42 | 0.38 | 0.47 |
| 2.5 | 0.78 | 0.68 | 0.35 | 0.31 | 0.40 |

[a] $\gamma = [\mathrm{AIGlc}]_0/[\mathrm{BPEA}]_0$. [b] Fraction of reacted B* units as determined by $^1$H NMR before hydrolysis. [c] Fraction of reacted B* units as determined by $^1$H NMR after hydrolysis. [d] Degree of branching as determined by $^1$H NMR using eq 2 before hydrolysis. [e] Degree of branching as determined by $^1$H NMR using eq 2 after hydrolysis. [f] Theoretical degree of branching as determined using eq 3.

DB$_{\text{NMR}}$ decreases with $\gamma$, as predicated by calculations. In all the cases, however, the observed values are slightly lower than the calculated ones, which might be attributed to the simplifications made for the calculations, i.e., equal reacativity of A*, B*, and M* chain ends. Although NMR experiments afford a conclusive measurement of the degree of branching for lower $\gamma$ values, the low concentration of branch points in the copolymer at $\gamma > 5$ does not allow the determination of the degree of branching directly by the spectroscopic method because of low intensities of the peaks in the regions around 1.85 ppm and 1.0−1.3 ppm, as shown in Figure 9. However, for the case of high comonomer ratios, $\gamma \gg 1$, the relation between DB$_{\text{theo}}$ and $\gamma$ becomes very simple and does not depend on the reactivity ratios of the various active centers and is represented as DB$_{\text{theo}}$ $\approx 2/(\gamma + 1)$.[29] When the reactivities of the various active centers are not equal, the dependences are more complex, and the degree of branching may be higher or lower, depending upon the systems. In this copolymerization system, the rate constant of the sugar-carrying acrylate was comparatively lower than that of the normal acrylates, and longer polymerization time was required to attain almost full conversion. Hence, the rate constant of BPEA used as an AB* inimer should be different from that of the comonomer, AIGlc, used in this study. This could also lead to the formation of starlike structures instead of randomly branched ar-

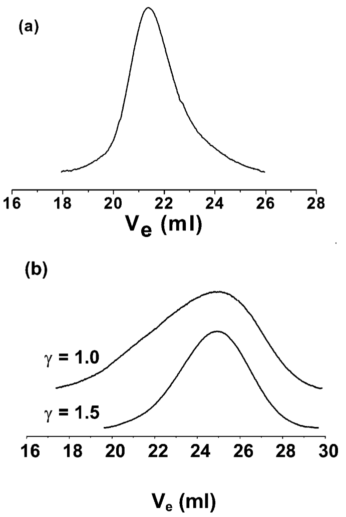


**Figure 10.** NMP phase GPC traces of (a) linear poly(AGlc) and (b) branched poly(AGlc)s.

chitectures. A detailed investigation is now in progress and will be reported elsewhere.

**Deprotection of Linear and Branched Poly(AIGlc)s.** The hydrolysis of the isopropylidene groups in the linear and branched poly(AIGlc)s was performed by treating the samples with formic acid.[22] The final product was obtained by freeze-drying from dioxane after the deprotected polymer was dialyzed against water. Figure 9a reveals that the signals of the isopropylidene protons (1.2−1.4 ppm) completely disappear after the hydrolysis of the linear poly(AIGlc), and a broad signal assignable to anomeric hydroxyl groups of the sugar moieties (6.4−7.0 ppm) appears. This proves that the deprotection proceeds quantitatively. The linear deprotected polymers, poly(3-*O*-acryloyl-α,*β*-D-glucopyranoside), which can be abbreviated as poly(AGlc), are white powders completely soluble in water, methanol, and DMSO but insoluble in THF and acetone. For the branched poly(AGlc)s, the solubility of the polymers were dependent upon the comonomer ratios, $\gamma$. In the case of $\gamma = 1$, the branched poly(AGlc) was partially soluble in water, which is attributed to the 50% of the nonpolar inimer segment. From $\gamma = 1.5$ onward, the polymers were completely soluble in water, DMSO, and methanol but insoluble in THF and acetone. It is important to note that the unchanged resonance signal of protons of the ethylene linkage and those geminal to bromine at 4.0−4.6 ppm suggests that the BPEA composition in the branched poly(AGlc) is almost the same as that in branched poly(AIGlc). As mentioned in the previous section, the fraction of b units (reacted B* units) and $DB_{NMR}$ after the hydrolysis are in good agreement with those of the branched poly(AIGlc)s. These results also indicate that the branched structure is intact during the complete deprotection of the isopropylidene groups and proceeds selectively to yield characteristic branched poly(AGlc)s.

Figure 10 represents the NMP-phase GPC traces of the linear and branched poly(AGlc)s. The hyperbranched samples show a broad distribution and comparable molecular weights as observed in THF-phase GPC before the hydrolysis. The molecular weights and molecular weight distributions for the hydrolyzed branched poly(AGlc)s at $\gamma = 1.0$ and 1.5 are $M_n = 7900$ ($M_w/M_n = 1.91$) and $M_n = 7300$ ($M_w/M_n = 1.40$), respectively. These results suggest that the molecular weights and the branched architecture of the hydrolyzed products correspond to those of the branched poly(AIGlc)s. The molecular weight and molecular weight distribution of the hydrolyzed homopolymer is $M_n = 22\,900$ ($M_w/M_n = 1.16$), which is fairly in agreement with $M_{n,calcd} = 23\,400$ and also with the results $M_n = 24\,200$ ($M_w/M_n = 1.14$) obtained before hydrolysis.

FT-IR spectra of the linear and branched poly(AGlc)s obtained after hydrolysis are shown in Figure S-2 (see Supporting Information). The absorption bands due to the isoproylidene groups are observed at 3000, 1450, and 1380 $cm^{-1}$ assigned to the C−H stretching and C−H asymmetric and symmetric deformation modes, respectively. The C−O stretching band of the isopropylidene group is also observed in the region between 1200 and 1000 $cm^{-1}$. After the deprotection, these bands disappear, and a strong absorption band around 3500 $cm^{-1}$ is observed due to the hydroxyl group formed by the deprotection. The spectrum of the branched poly(AGlc) at $\gamma = 2.5$ having less branch points is almost same as that of the linear poly(AGlc).

## Conclusions

Self-condensing vinyl copolymerization (SCVCP) of the sugar-carrying acrylate, AIGlc, with the acrylic AB* inimer via ATRP provides a straightforward strategy for generating water-soluble hyperbranched glycopolymers and their precursors. Linear poly(AIGlc) with controlled molecular weights and very low polydispersities ($1.05 < PDI < 1.14$) were obtained in a controlled fashion using the CuBr/PMDETA catalyst system. The significant influence of the bulky isopropylidene-protected sugar moiety in AIGlc was observed on the polymerization rate and the macroscopic quantities such as intrinsic viscosity and radius of gyration. It was found that a suitable choice of the polymerization conditions is required to obtain water-soluble glycopolymers with characteristic highly branched architectures, which can then be manipulated for various biological, pharmaceutical, and medical applications. Further studies on this interesting branched glycopolymers for such directions will be reported separately. This work broadens the scope of facile synthesis of branched glycopolymers by a controlled polymerization technique, in which the architecture can be simply manipulated by the nature and composition of sugar-carrying vinyl monomer used as a comonomer. Extension to planar and spherical polymer brushes is also planned.

**Acknowledgment.** We appreciate S. Wunder for her help with the GPC−viscosity measurements.

**Supporting Information Available:** Figures S-1 and S-2. This material is available free of charge via the Internet at http://pubs.acs.org.

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