Synthesis and Characterization of Hyperbranched $Poly(\epsilon$ -caprolactone)s Having Different Lengths of Homologous Backbone Segments

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ABSTRACT: Hyperbranched poly(ϵ -caprolactone)s (HPCLs) were synthesized by moisture-sensitive catalyst-free polycondensation of AB₂ macromonomers, 2,2-bis[ω -hydroxy oligo(ϵ -caprolactone)methyl]propionic acids. The HPCLs were designed to incorporate different lengths of linear oligomeric segments consisting of 5, 10, and 20 ϵ -caprolactone monomer units on the branched backbone chains, accordingly named as HPCL-5, -10, and -20, respectively. End-group analyses were performed on ¹H NMR spectra of the three HPCLs, which provided information about the average number of ϵ -caprolactone units incorporated in the AB₂ macromonomers and thus the average number of AB₂ macromonomer units incorporated in the resulting hyperbranched polymers. Consequently, the absolute values of molecular weights for the HPCLs were calculated. Size exclusion chromatography equipped with multiangle laser light scattering detector (SEC-MALLS) was employed to measure absolute molecular weights and molecular weight distributions of HPCLs. Then, the results were compared with those obtained from 'H NMR end-group analyses, indicating that there was a good agreement between them. From small-angle X-ray scattering (SAXS), the radii of gyration of the HPČLs and their linear counterpart, poly(ϵ caprolactone) (LPCL), were determined from the initial slope of the reciprocal of scattered intensity, 1/I(q), vs the square of scattering vector, q^2 , curves, fit by the Zimm scattering function. The ratio of mean-square radius of gyration of each HPCL to that of LPCL, termed the branching ratio, resulted in the relative degree of branching for individual HPCLs. As the length of linear oligo(ϵ -caprolactone) segments decreased, the more highly branched polymers were obtained, i.e., in the order of HPCL-5, -10, and -20 from higher to lower degree of branching. The melting temperatures of HPCLs were lower than that of LPCL and decreased with increase in the degree of branching. In contrast, the thermal decomposition temperatures of HPCLs were shown to be higher than that of LPCL, becoming higher as the degree of branching increased.

Introduction

Recently, hyperbranched polymers have received considerable attention due to the expectation that their highly branched structure will impart unique physical and chemical properties.¹⁻⁵ Hyperbranched polymers may be considered as irregular analogues of the dendrimers that have well-defined and perfectly branched structure. Although dendrimers are prepared through divergent or convergent approaches that are composed of step-by-step synthesis, hyperbranched polymers are prepared by direct one-pot polymerization of AB_x-type monomers.⁶ This synthetic simplicity along with the fact that many of the physical/mechanical properties of both hyperbranched polymers and dendrimers have been reported to be similar when possessing the same repeating units⁷ has encouraged many researchers to develop tailor-made materials for a specific application where high performance and/or novel functionality are needed. Trollsas et al. have reported the synthesis of hyperbranched poly(ϵ -caprolactone)s (HPCLs) from polyesterification of homologous AB₂ macromonomers with different lengths of linear oligo(ϵ -caprolactone)s using 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS) and 1,3-dicyclohexylcarbodiimide (DCC) as catalysts.⁸ This novel synthetic approach was shown to allow production of a homologous series of hyperbranched

polymers with a range of structural variations such as different lengths of incorporated $oligo(\epsilon$ -caprolactone) segments.⁸ Recently, Skaria et al. have reported a new synthetic concept, the enzyme-catalyzed synthesis of HPCLs.⁹ This synthetic route enables to skip multistep reactions of preparing AB₂ macromonomers in the synthesis of HPCLs of Trollsas et al. However, these two HPCLs have the distinct difference in the chain structure. The HPCLs of Skaria et al. have randomly incorporated oligo(ϵ -caprolactone) segments, while rather precisely controlled and readily characterizable oligo-(ϵ -caprolactone) segments are incorporated in the HP-CLs of Trollsas et al., which is more preferable in combining the properties of conventional linear polymers with the new properties of hyperbranched polymers and in investigating the effects of structural variables such as branching and the length of incorporated $oligo(\epsilon$ -caprolactone) segments on the resulting HPCLs. Nevertheless, it is more desirable to modify the original synthetic route into an alternative one such as a moisture-sensitive catalyst-free polyesterification in order to be applicable to the industrial scale production with easier process control for its further practical application such as ecologically friendly polymeric additives.

Determination of the degree of branching in hyperbranched polymers is one of prerequisites to describe their structural features as well as to correlate the structure with their properties.^{10,11} The average degree

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of branching (DB), the term first proposed by Fréchet et al.,¹² is commonly calculated as the sum of the terminal and dendritic units divided by the total sum of all repeating units as the following equation:

$$DB = \frac{\sum D + \sum T}{\sum D + \sum L + \sum T}$$
(1)

where ΣD , ΣT , and ΣL are the numbers of dendritically, terminally, and linearly incorporated monomer units in the hyperbranched polymers. Determination of DB is usually limited to some cases in which the fractions of each component (D, L, T) are distinguishable, mostly observable with the spectroscopic methods.¹³ Otherwise, an alternative approach to obtain information about DB is possible from measurements of the dimensions of the hyperbranched polymer molecules with reference to their linear analogue, recognizing that the DB is a matter of relativeness of the partially branched to the completely linear structure. The hyperbranched polymer chains are, in general, less densely packed than the linear of the same molecular weight in the solid state due to their amorphous nature. However, in the completely dissolved solution state, the dimensions of the linear polymers become larger than those of the branched molecules of the same molecular weight because the entangled chains and the crystalline regions get dissolved to be free of any restricting force and to make the molecular size larger, while the branched molecules are less solvated due to the chemically bonded branched structure.¹⁴ Moreover, the higher the DB, the smaller the dimensional size among the hyperbranched polymers of the same chemical structure and the analogous molecular weights. Thus, the ratio of the mean-square radius of gyration of the given hyperbranched polymer to that of its linear analogue, termed as branching ratio, g, provides an alternative means to characterize the branching structure and hence obtain information about relative DBs among the homologous series of hyperbranched polymers:¹⁵

$$g = \frac{\langle R_{\rm g}^2 \rangle_{\rm branched}}{\langle R_{\rm g}^2 \rangle_{\rm linear}}$$
(2)

In the present study, hyperbranched $poly(\epsilon$ -caprolactone)s (HPCLs) having different lengths of linear oligo(ϵ -caprolactone) segments incorporated in their branched backbone chains are synthesized by a vacuum melt polycondensation reaction free from using moisturesensitive catalysts. Then, the average number of ϵ caprolactone monomer units in AB2 macromonomers $\langle \hat{N}_{\epsilon-\text{CL}} \rangle$, the average number of AB₂ macromonomers in HPCLs $\langle N_{AB_2} \rangle$, and the resulting absolute value of number-average molecular weights of the HPCLs are determined by end-group analyses on ¹H nuclear magnetic resonance (NMR) spectra. These results are then compared and confirmed with the absolute molecular weights and molecular weight distribution of the HPCLs determined by means of size exclusion chromatography (SEC) equipped with multiangle laser light scattering (MALLS) detector. To analyze the degree of branching, the branching ratio among the HPCLs is compared, in which the absolute values of radius of gyration for both HPCLs and LPCL are obtained from small-angle X-ray scattering (SAXS) experiments. Another focal point of



this study is to investigate the thermal characteristics of HPCLs in conjunction with their branching features.

Experimental Section

Materials. 2,2-Bis(hydroxymethyl)propionic acid (bis-MPA, 98%), potassium hydroxide (KOH, 99%), benzyl bromide (98%), ϵ -caprolactone (99%), palladium on activated carbon (Pd/C, 5 wt % palladium), tin(II) 2-ethylhexanoate (Sn(Oct)₂, 99%), and *p*-toluenesulfonic acid (TSA, 98.5%) were purchased from Aldrich Chemical, being used as received. *N*,*N*-Dimethylformamide (DMF, 99%), diethyl ether (99%), toluene (99%), methanol (MeOH, 99%), tetrahydrofuran (THF, 99%), and ethyl acetate (EtOAc, 99%) were purchased from Daejung Chemicals & Metals (Korea) and used without further purification. Linear poly(ϵ -caprolactone) (LPCL), as a linear counterpart of the hyperbranched poly(ϵ -caprolactone) (HPCLs) prepared in this study, was reported by the supplier (Aldrich Chemical) to have number-average molecular weight, *M*_n, of 10 000.

Synthesis. 2,2-Bis(hydroxymethyl)propyl Benzoate, 1. 27 g (200 mmol) of bis-MPA and 12.9 g (230 mmol) of KOH were dissolved in 150 mL of DMF, and the potassium salt was allowed to form by stirring reaction mixture at 100 °C for 1 h. Benzyl bromide (42.4 g) was then added dropwise to a solution, and the mixture was stirred and allowed to react with maintaining temperature for 15 h. After completion of the reaction, the solvent was evaporated; the residue was dissolved in 600 mL of diethyl ether and extracted with distilled water (3 × 150 mL). The crude product was then purified by recrystallization from toluene to give 2,2-bis(hydroxymethyl)-propyl benzoate, **1** (Scheme 1), as white crystals. Yield: 65%. The structural verification has been described elsewhere.^{16,17}

Ring-Opening Polymerization of ϵ -**Caprolactone.** 2,2-Bis[ω -hydroxy oligo(ϵ -caprolactone)methyl]propyl benzoate (benzyl protected AB₂ macromonomer), **2**, was synthesized by ringopening polymerization which was initiated with **1** using a catalytic amount of Sn(Oct)₂. The target number of ϵ -caprolactone monomer units incorporated in **2** was determined by the monomer-to-initiating hydroxyl group molar ratio. The reaction was carried out in the melt at 110 °C for 20 h. The crude product was then dissolved in THF and precipitated into cold MeOH to give **2** as white solids. Yield: 92–96%. The complete polymerization procedure and the structural verification of **2** have been reported elsewhere.⁸

Hydrogenation. 2,2-Bis[ω -hydroxy oligo(ϵ -caprolactone)methyl]propionic acid (α -carboxylic- ω -dihydroxy AB₂ macromonomer), **3**, was obtained by hydrogenation reaction of **2** using a Pd/C catalyst. Hydrogenation reaction was carried out in a solution of **2** in THF/EtOAc (20/80, v/v) mixed solvent. After the Pd/C (10 wt % to **2**) was added to a solution, the reaction vessel was evacuated and put under a hydrogen (H₂)



Figure 1. ¹H NMR spectrum (300 MHz) of hyperbranched poly(*\epsilon*-caprolactone)s (HPCLs).

atmosphere. The reaction was stopped after 24 h, and the Pd/C was filtered off. The reaction mixture was concentrated by evaporation of solvent and then poured into cold MeOH to give **3** as white solids. The AB₂ macromonomers in the above were designed to possess different lengths of linear oligomeric segments consisting of 5, 10, and 20 ϵ -caprolactone units; they were designated as AB₂-5, -10, and -20, respectively. Yield: 88–97%. The structural verification has been described else where.⁸

Polycondensation with Continuous Water Removal. Hyperbranched poly(ϵ -caprolactone)s (HPCLs), **4**, were synthesized by polycondensation with continuous water removal reaction of 3. Then, 3 and TSA were carefully mixed in a threenecked flask equipped with an argon inlet, a drying tube, and a stirrer. The mixture was allowed to react at 110 °C under a stream of argon, removing the water formed during the reaction. After 2 h, the argon stream was stopped purging, and the flask was sealed and connected to a vacuum line (10 Torr, cooling trap) for 3 h. After polycondensation reaction was completed, the mixture was dissolved in THF and precipitated into MeOH to give **4** as white solids. On the basis of the AB_2 macromonomers of different lengths of oligomeric ϵ -caprolactone segments used for syntheses, the resulting HPCLs were accordingly named as HPCL-5, -10, and -20, respectively. Yield: 87–94%. ¹H NMR (CDCl₃): Figure 1.

Characterization. ¹**H NMR Analysis.** The chemical structures of synthesized HPCLs were elucidated by ¹H NMR spectroscopy, employing a Bruker Avance DPX-300 spectrometer with the tetramethylsilane (TMS) proton signal as an internal standard in CDCl₃. ¹H NMR spectra was also analyzed to determine the average number of ϵ -caprolactone monomer units incorporated in AB₂ macromonomers, $\langle N_{\epsilon-\rm CL} \rangle$, the average number of AB₂ macromonomer units incorporated in HPCLs, $\langle N_{\rm AB_2} \rangle$, and consequently the number-average molecular weights of HPCLs, $M_{n,\rm NMR}$. The methods for determining the values of $\langle N_{\epsilon-\rm CL} \rangle$, $\langle N_{\rm AB_2} \rangle$, and $M_{n,\rm NMR}$ were explained in detail in the Results and Discussion section.

Measurement of Differential Refractive Index Increment, dn/dc. The dn/dc was measured with a Wyatt Optilab DSP interferometric differential refractometer at 690 nm at room temperature for the five concentrations (1 mg/mL < c < 9 mg/mL) of poly(ϵ -caprolactone) in a mixed solvent (THF/DMF 10/1 v/v; LiNO₃ 2 g/L). The dn/dc value was determined with the following relationship:^{18,19}

$$dn/dc = k d(\Delta V)/dc$$
(3)

where k is an instrument calibration constant and ΔV is the refractive index detector voltage. The k value was determined to be 1.56 \times 10⁻⁴ with standard sodium chloride (NaCl) samples at the wavelength of 690 nm, 25 °C.

Size Exclusion Chromatography with Multiangle Laser Light Scattering (SEC-MALLS). A size exclusion chromatography (SEC) modular system consisted of a Dionex DG-1210 degasser, a Dionex P680 HPLC pump, a Dionex automatic sample injector, and sets of five size exclusion columns (Ultramicro Styragel, $10^5 \times 2$, 10^4 , 10^3 , 500 Å) was used. A MiniDAWN (Wyatt Technology) multiangle laser light scattering (MALLS) detector equipped with 690 nm semiconductor laser was connected between the size exclusion columns and a Wyatt Optilab DSP differential refractometer. The mixed solvent of THF, DMF, and lithium nitrate (LiNO₃) was used as a mobile phase at a flow rate of 1.0 mL/min. A 100 μ L sample of a 0.1 mg/mL solution, which was filtered through a 0.2 μ m Whattman filter prior to use, was injected for all measurements. The software Astra (ver. 4.90.04, Wyatt Technology) was used to compute the calibration curves and the molecular weights distribution. The calibration of detectors was achieved using polystyrene standards of narrow molecular weight distribution with known molecular weights.

Small-Angle X-ray Scattering (SAXS). The radii of gyration, $R_{\rm g}$, of HPCLs and LPCL, which were too small to be measured by SEC-MALLS, were determined from SAXS. The SAXS intensity distribution, I(q), was measured with a rotating-anode X-ray generator (Bruker AXS Nanostar) operated at 40 kV and 35 mA. The X-ray source was monochromatized Cu K α ($\lambda = 1.54$ Å) radiation, and the scattering angle ranges between 0.5° and 2.5°. For the measurement, sample solutions (1 mg/mL) in THF were injected into glass capillary in liquid sample holder frame. The background correction was carried out using pure THF solvent. The values of $R_{\rm g}$ were estimated by curve fitting of reciprocal plots of I(q) as a function of q with the Zimm scattering function, which is described in detail later.

Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA). The melting temperatures, $T_{\rm m}$'s, of HPCLs and LPCL were determined by DSC with a TA Instruments DSC 2920 at heating rates of 10 °C/min under a nitrogen atmosphere. The temperatures with 10% weight loss of the polymers, $T_{\rm d10}$'s, were determined by TGA with a TA Instruments TGA 2050 at the heating rate of 10 °C/min under a nitrogen atmosphere.

Results and Discussion

The AB₂-type macromonomers, 2,2-bis[ω -hydroxy oligo-(ϵ -caprolactone) methyl]propionic acids, **3**, used for the preparation of hyperbranched poly(ϵ -caprolactone)s (HP-CLs), **4**, were synthesized according to a reaction developed by Trollsa's et al.⁸ The recipe and the method for the synthesis of HPCLs were, however, modified from those of Trollsa's et al., considering the applicability to the industrial scale production wherein the syntheses must be much less sensitive to the moisture. Table 1 summarizes the conditions for the preparation of AB₂ macromonomers and HPCLs. Ring-opening polymerization with variable ϵ -caprolactone-to-initiating hydroxyl group molar ratios ([ϵ -CL]₀/[-OH]₀ = 5, 10, and 20), followed by hydrogenation reaction, produced three different AB₂ macromonomers (i.e., AB₂-5, -10, and -20),

 Table 1. Preparation of AB2 Macromonomers and Hyperbranched Poly(<-caprolactone)s</td>

sample	[€-CL]₀/ [−OH]₀ ^a	macro- monomer entry	$\langle N_{\epsilon\text{-CL}} angle^b$	$\langle N_{{ m AB}_2} angle^c$	M _{n,NMR}	yield (%)
AB ₂ -5	5		5.7		1435	88
AB ₂ -10	10		10.3		2485	94
AB ₂ -20	20		20.1		4720	97
HPCL-5		AB_2-5		8.1	11510	87
HPCL-10		AB ₂ -10		5.1	12700	94
HPCL-20		AB_2-20		3.3	15100	92

 a ϵ -Caprolactone monomer-to-initiating hydroxyl group molar ratio. b Average number of ϵ -caprolactone units incorporated in AB₂ macromonomers determined by ¹H NMR. c Average number of AB₂ macromonomer units incorporated in HPCLs determined by ¹H NMR. d Water/methanol (50/50, v/v)-insoluble part for AB₂-5 and cold methanol-insoluble part for the other samples.



Figure 2. ¹H NMR spectra focusing the peaks of the chain ends (E and E') and of the repeating methylene units (R and R') in AB₂ macromonomers (top) and hyperbranched $poly(\epsilon-caprolactone)s$ (bottom).

3, having different lengths of linear $oligo(\epsilon$ -caprolactone)s. The HPCLs were successfully produced from 3 by polycondensation with continuous water removal with *p*-toluenesulfonic acid (TSA), which was known to be effective for the syntheses of hyperbranched polyesters with the lower sensitivity to the moisture²⁰ compared to 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS)/1,3-dicyclohexylcarbodiimide (DCC) catalyst system reported previously.8 The 1H NMR spectra of both AB2 macromonomers and HPCLs were analyzed to determine the average number of ϵ -caprolactone monomer units incorporated in AB₂ macromonomers, $\langle N_{\epsilon-\text{CL}} \rangle$, and the average number of AB2 macromonomer units incorporated in HPCLs, $\langle N_{AB_2} \rangle$. As shown in Figure 2, the peak assigned to the chain ends (E, $-CH_2OH$, δ 3.59) and the peak corresponding to the repeating methylene units (R, $-COCH_2$, δ 2.22) are quite distinguishable. Thus, the $\langle N_{\epsilon-\text{CL}} \rangle$ values of AB₂ macromonomers could be readily calculated from the ratios of the integrated area of peak R to that of peak E (Figure 2, top), which were in close agreement with those of targeted values solely predictable from $[\epsilon\text{-}CL]_0/[-OH]_0$ ratios (Table 1). In a similar manner, the values of $\langle N_{AB_2}\rangle$ of HPCLs were calculated from the following equation based on the branching theories developed by Flory:^{21}

$$\langle N_{\rm AB_2} \rangle = \frac{m}{2 \langle N_{\epsilon-\rm CL} \rangle - m} \tag{4}$$

where *m* represents the ratios of the integrated area of peak R' to the integrated area of peak E' of HPCLs (Figure 2, bottom). Consequently, the number-average molecular weights of AB₂ macromonomers and HPCLs were calculated from the following equation and also listed in Table 1 along with the results of $\langle N_{\epsilon-CL} \rangle$ and $\langle N_{AB_2} \rangle$:

$$M_{\rm n NMR}(AB_2 - n) = MW_{\rm his-MPA} + 2MW_{\epsilon-CI} \langle N_{\epsilon-CI} \rangle$$
 (5)

$$M_{n,NMR}(HPCL-n) = M_{n,NMR}(AB_2-n)\langle N_{AB_2}\rangle + MW_{H_2O}[\langle N_{AB_2}\rangle - 1]$$
(6)

where $MW_{bis\text{-}MPA}$, $MW_{\epsilon\text{-}CL}$, and MW_{H_2O} are the molecular weights of bis-MPA, $\epsilon\text{-}caprolactone,$ and water, respectively. From the molecular weight data of HPCLs prepared in the same condition, it was found that larger macromonomers produced slightly lower molecular weight HPCLs (Table 1). The decrease in the reactivity of larger macromonomers can be explained by increase in the steric hindrance as well as decrease in the concentration of reacting sites in a unit volume.

To prove and confirm the results from ¹H NMR endgroup analyses, a size exclusion chromatography (SEC) with multiangle laser light scattering (MALLS) detector was employed as an another means to obtain absolute information about molecular weights. From an SEC, the smooth and monomodal chromatograms were observed for all of AB₂ macromonomers and HPCLs as illustrated in Figure 3a for AB₂-10 and HPCL-10. Compared in Figure 3b are the concentration chromatograms of three HPCLs and LPCL; although the molecular weight of HPCL-20 was higher than that of LPCL on the basis of determination from ¹H NMR end-group analyses, their chromatograms were shown in the almost same retention volume area. Such unexpectedness that usually occurs in characterizing molecular weights of hyperbranched polymers with gel permeation chromatography is generally ascribed to the inevitable decrease in hydrodynamic volume imposed by branching,²² which in turn exceeds the relative discrepancy with the polystyrene standard.²³ The same trend was also found in the cases of HPCL-5 and -10; even though the molecular weights of the two HPCLs determined by endgroup analyses were quite similar to that of LPCL, their chromatograms lay on the higher retention volume area relative to the LPCL. This also indicates the smaller hydrodynamic volumes of HPCL-5 and -10 than that of LPCL, despite the almost similar molecular weights. An SEC equipped with MALLS detector overcomes such limitation typically brought about by the conventional SEC for hyperbranched polymers and dendrimers.

In MALLS detecting, the angular dependence of the excess absolute time-average scattered light intensity, known as the excess Rayleigh ratio $R(\theta)$, of a dilute polymer solution at concentration C (g/mL) and the



Figure 3. Size exclusion chromatograms of typical AB₂ macromonomer and hyperbranched poly(ϵ -caprolactone) (a) and of all three hyperbranched poly(ϵ -caprolactone)s (HPCL-5, -10, and -20) and linear poly(ϵ -caprolactone) (b).

scattering angle θ was measured. The Rayleigh ratio, $R(\theta)$, is defined as²²

$$R(\theta) = \frac{(I_{\theta} - I_{\theta,\text{solvent}})r^2}{I_0 V} = f \frac{I_{\theta} - I_{\theta,\text{solvent}}}{I_0} \qquad (7)$$

where I_{θ} is the intensity of light scattered in the direction at an angle θ to the incident light. I_0 , $I_{\theta,\text{solvent}}$, V, r, and f are the intensity of the incident light, the scattered intensity of the solvent, the scattering volume, the distance between the scattering volume and the detector, and an instrumental calibration constant, respectively. The value of $R(\theta)$ is related to the molar mass M, root-mean-square radius $\langle R_g^2 \rangle^{1/2}$ (equivalently called the radius of gyration, R_g), and concentration C as following the Zimm formalism of the Rayleigh– Debye–Gans light scattering model:^{19,22}

$$\frac{KC}{R(\theta)} \simeq \frac{1}{M} \frac{1}{P(\theta)} + 2A_2C = \frac{1}{M} \left(1 + \frac{16\pi^2}{3\lambda^2} \sin^2\left(\frac{\theta}{2}\right)\right) + 2A_2C$$
(8)

where θ , $P(\theta)$, A_2 , and λ are the scattering angle, the particle scattering function, the second virial coefficient,

Table 2. Molecular Weight Data for Hyperbranched Poly(ε-caprolactone)s (HPCLs) and Linear Poly(ε-caprolactone) (LPCL) Determined by ¹H NMR End-Group Analysis, Conventional SEC, and SEC with MALLS Detector

	¹ H NMR SEC					
sample	$M_{\rm n,NMR}$	$M_{n,SEC}$	$M_{\rm w}/M_{\rm n}$	$M_{n,MALLS}$	$M_{\rm w,MALLS}$	$M_{\rm w}/M_{\rm n}$
HPCL-5	11 510	8 300	1.7	11 800	20 900	1.8
HPCL-10	12 700	9 500	1.6	12 600	20 400	1.6
HPCL-20	15 100	10 500	1.6	15 700	24 200	1.5
LPCL	10 100	10 200	1.4	10 700	15 200	1.4

and the wavelength of light, respectively. The optical constant K is given by

$$K = \frac{4\pi^2 n_0^2}{\lambda^4 N_h} \left(\frac{\mathrm{d}n}{\mathrm{d}C}\right)^2 \tag{9}$$

with n_0 , N_A and dn/dC being the refractive index of the solvent at the given wavelength, Avogadro's number, and the specific refractive index increment of the polymer in the given solvent at the given wavelength. The value of dn/dC was determined beforehand in a separate experiment with the five concentrations of poly(ϵ -caprolactone) solutions (1 < *C* < 9 mg/mL) in the solvent (THF/DMF 10/1 v/v; LiNO₃ 2 g/L) at the wavelength (690 nm) used for SEC-MALLS measurements. From the plot of ΔV vs concentration, the d*n*/d*C* value was obtained to be 0.0652. In SEC-MALLS measurements, the sample concentrations for each data slice (C_i) are determined from concentration detector output, and the molecular weights for each data slice (M_i) are determined from the $KC/R(\theta)$ vs sin²($\theta/2$) plot (Debye plot). With the values of C_i and M_i for each data slice along the entire chromatogram, the numberaverage molecular weights and weight-average molecular weights were calculated from the following relationship:

$$M_{\rm n,MALLS} = \frac{\sum C_i}{\sum C_i M_i}$$
(10)

$$M_{\rm w,MALLS} = \frac{\sum C_i M_i}{\sum C_i} \tag{11}$$

Thus, the absolute molecular weights and the polydispersity index determined by the SEC-MALLS are summarized in Table 2, the results from ¹H NMR end-group analysis and SEC being also listed for comparison. For the HPCLs, the number-average molecular weights determined by SEC-MALLS, $M_{n,MALLS}$, were found to be in good agreement with those of ¹H NMR end-group analysis, $M_{n,NMR}$. Whereas, the results from conventional SEC, $M_{n,SEC}$, showed deviation from the values of $M_{n,MALLS}$ and $M_{n,MNMR}$ as was expected.

Another important material characteristic to be characterized to describe the structural features of the hyperbranched polymers is the degree of branching (DB). The DB is commonly determined from the relative proportions among the NMR resonance peak areas pertinent to the respective dendritic (D), linear (L), and terminal (T) units of the given hyperbranched polymer whenever there exist the distinguishable corresponding chemical shifts. In some previous articles, the DB of the HPCLs were determined from the chemical shifts of the characteristic peaks of the methyl group of the bis-MPA

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corresponding to each D, L, and T unit.^{8,9} However, the chemical environments of the methyl group among D, L, and T units in the HPCLs of the present study were not significantly different due to intrinsically attached long oligo(ϵ -caprolactone) segments, which made the HPCLs of the present study show neither distinguishable ¹H resonance peaks useful for the calculation of DB nor quaternary carbons unique for the determination of DB. In such a case, information about DB can be alternatively achieved from measurements of the dimensions of the hyperbranched polymer molecules with reference to their linear analogue, recognizing that the DB is a matter of relativeness of the partially branched to the completely linear structure. One possible method is based on the plots of a radius of gyration against molecular weight directly measurable from SEC-MALLS,^{24,25} in which information about DB can be inferred from the values (less than 0.5) of the slope in the plots. However, the radii of gyration of the three HPCLs were found to be too small to be exactly measured from the SEC-MALLS. Therefore, it seeks another approach to measure the radius of gyration by means of a small-angle X-ray scattering (SAXS) and then determine the branching ratio, g, which denotes the ratio of mean-square radii of gyration between a given HPCL and the reference linear $poly(\epsilon$ -caprolactone). It is noteworthy that the parameter g is always less than 1 and decreases with increase in the degree of branching because the branched molecules become more compactly packed rather than the more loosely branched molecules or the corresponding linear counterpart of the similar molecular weight in the completely dissolved solution state.²² Scattering curves obtained from polymer solutions, after corrections for instrumental effects, generally consist of scattering contributions from the single particle scattering, molecular size and shape of a single particle, and interparticle interference. Thus, the scattering from a group of particles can be expressed in terms of

$$I(q) = kNP(q) S(q)$$
(12)

where I(q) is the experimental scattered intensity, *q* is the scattering vector, k is an electron density contrast factor, N is the number of particles, P(q) is the single particle scattering function, and S(q) is the interparticle scattering function.²⁶ Assuming that the sample solutions of HPCLs and LPCL ($C_{polymer} = 1 \text{ mg/mL}$) were very dilute and in a noninteracting system, the interparticle scattering effect can be ignored (i.e., $S(q) \rightarrow 1$), providing scattering information solely from the particle scattering functions. The most common method for determining the radius of gyration, R_{g} , from scattering data is classified into the graphical techniques known as the Zimm²⁷ and Guinier²⁸ methods, which involve the plot of either 1/I(q) or $\ln I(q)$ vs q^2 . Figure 5 is the typical scattering curves for HPCLs observed by SAXS, although those only for HPCL-10 was shown here; the Zimm plot (a) is represented as 1/I(q) vs q^2 and the Guinier plot (b) as $\ln I(q)$ vs q^2 . For the Zimm plot in Figure 5a, the HPCL-10 appeared linear over a relatively large q range, while the HPCL-10 for the Guinier plot had extremely strong curvature near the origin as shown in Figure 5b. When data for $qR_g \ll 1$ are available, $R_{\rm g}$ can be easily extracted from the initial slope of the curve at q = 0 in Zimm and/or Guinier plot, with all of these methods giving equivalent $R_{\rm g}$ values in this limit. However, when experimental data



Figure 4. Plot of ΔV vs concentration (g/mL) for poly(ϵ -caprolactone) in THF/DMF/LiNO₃ mixed solvent at 690 nm.



Figure 5. Small-angle X-ray scattering (SAXS) profiles of hyperbranched poly(ϵ -caprolactone) (HPCL-10): Zimm plot (a) and Guinier plot (b). The dashed lines indicate the fits to eqs 14 and 15, respectively.

are only available for higher q values, the determination of $R_{\rm g}$ becomes rather model dependent.^{25,26} With regard to the SAXS experiments in this work, the entire accessible q range varied from $q_{\rm min} = \sim 0.036$ to ~ 0.177 , and the region of the particle scattering term varied from $q_{\rm min}R_{\rm g} = \sim 1.6$ for the smallest particles to ~ 1.9 for the largest, which means a simple estimation of $R_{\rm g}$ based on expansions about q = 0 may be inappropriate. An alternative approach to extract $R_{\rm g}$ values from

Table 3. Radius of Gyration (R_g) , Branching Ratio (g), Melting (T_m) and Degradation (T_{d10}) Temperature, Enthalpy of Melting (ΔH_m) , and Degree of Crystallinity (X_c) of Hyperbranched Poly(ϵ -caprolactone)s (HPCLs) and Linear Poly(ϵ -caprolactone) (LPCL)

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sample	$R_{ m g}$ (nm) ^a	g	$T_{\rm m}$ (°C) ^b	$\Delta H_{\rm m}$ (J/g) ^b	X _c (%)	T_{d10} (°C) ^c
HPCL-5 HPCL-10 HPCL-20 LPCL	4.57 4.77 5.18 5.23	0.76 0.83 0.98 1	44 49 52 57	67.7 75.4 78.8 80.2	49.6 55.3 57.8 58.8	354 348 342 331

^{*a*} Determined from SAXS curves fit by the Zimm scattering function. ^{*b*} DSC melting transition observed on second heating. ^{*c*} Temperature of 10% weight loss.

scattering curves obtained over the relatively larger qR_g region is performing weighted nonlinear, least-squares fits to the scattering curves over the q range, $[q_{\min}, q_{\max}]$:

$$I(q) = AP(R_{g}, q) + B, [q_{\min}, q_{\max}]$$
 (13)

Previous results by Prosa et al.²⁶ revealed that the scattering curves of hyperbranched polymers are fit much better by particle scattering function suggested by Zimm, $P_{\text{Zimm}}(q)$, while those of dendrimers are fit better by Guinier function, $P_{\text{Guinier}}(q)$. Particle scattering functions suggested by Zimm and Guinier are as follows:

$$P_{\text{Zimm}}(R_{\text{g}},q) = 1/\left(1 + \frac{q^2 R_{\text{g}}^2}{3}\right)$$
 (14)

$$P_{\text{Guinier}}(R_{\text{g}}, q) = \exp\left(-\frac{q^2 R_{\text{g}}^2}{3}\right)$$
(15)

As shown in Figure 4, the Zimm fit was more accurate appearing linear over the larger q range than the Guinier fit for the HPCLs, which was well agreeable with the previous results by Prosa et al. Summarized in Table 3 are the $R_{\rm g}$ values of all three HPCLs and LPCL determined by curve fitting of the Zimm plots with P_{Zimm} as well as branching ratios, g's, subsequently determined from the mean-square values of $R_{\rm g}$. The g values were shown to decrease in the order of HPCL-20, -10, and -5 from the value of 1.0 for LPCL, indicating that the relative degree of branching increased as the length of linear oligo(ϵ -caprolactone) segments incorporated in the backbone chains became shortened. These are in accordance with the predictions from the value of $\langle N_{AB_2} \rangle$ in Table 1 because the HPCLs obtained from the smaller macromonomers have more numbers of intrinsic branching points when all the HPCLs have similar molecular weights.

As the length of linear oligo(ϵ -caprolactone) segments affected considerably the degree of branching in the resulting HPCLs, their thermal transition and degradation characterized with DSC and TGA were found to be also dependent on this structural variation. Figure 6 represents the DSC thermograms of HPCLs and LPCL with appearance in sharp melting transition peaks. The melting temperatures, T_m 's, of HPCLs are all lower than that of LPCL and gradually decreased as the degree of branching became increased, which is expected because the presence of branches in a polymer may render crystallization more difficult than in a linear polymer.²⁹ The degrees of crystallinity (X_c 's) of HPCLs as well as



Figure 6. DSC thermograms of hyperbranched $poly(\epsilon$ -caprolactone)s and linear $poly(\epsilon$ -caprolactone).



Figure 7. TGA thermograms of hyperbranched $poly(\epsilon$ -caprolactone)s and linear $poly(\epsilon$ -caprolactone).

LPCL were determined from the enthalpy of melting using the following equation:

$$X_{\rm c} (\%) = \frac{\Delta H_{\rm m}}{\Delta H_{\rm m}^{0}} \times 100 \tag{16}$$

where $\Delta H_{\rm m}$ is the apparent enthalpy of melting of each samples and $\Delta H_{\rm m}^{0}$ is the extrapolated value of enthalpy corresponding to the melting of a 100% crystalline poly-(ϵ -caprolactone), which was previously reported to be 136.4 J/g.³⁰ As listed in Table 3, X_c 's decreased, and thus the amorphous fraction in the samples increased, with increase in the degree of branching. However, the temperatures of 10% weight loss, T_{d10} 's, of HPCLs and LPCL, determined from TGA thermograms in Figure 7 and summarized in Table 3, indicated a reverse trend compared to the $T_{\rm m}$'s. This observation in increase of thermal stability for the HPCLs relative to the LPCL has motivated our further study in that determination of the polymer chain mobility may correlate with and explain the increase of thermal stability endowed by branching as well as how the degree of branching may affect the crystallization behavior of the HPCLs in conjunction with the thermal degradation, which will be of the near future.

Conclusion

1. A series of hyperbranched $poly(\epsilon$ -caprolactone)s (HPCLs) with homologous structural variation in the backbone chains were synthesized through moisturesensitive catalyst-free polycondensation with continuous water removal of AB₂ macromonomers, 2,2-bis[ω -hydroxy oligo(ϵ -caprolactone)methyl] propionic acids, having different lengths of oligometric ϵ -caprolactone segments. The targeted structural variation, which was the oligometric segments consisted of 5, 10, and 20 ϵ -caprolactone monomer units, were confirmed by calculating the average number of ϵ -caprolactone units present AB₂ macromonomer, $\langle N_{\epsilon-\text{CL}} \rangle$, from ¹H NMR spectra.

2. The molecular weights of the resulting HPCLs with respect to their linear counterpart, LPCL, were determined by (1) end-group analysis on ¹H NMR spectra to calculate the average number of macromonomer units incorporated in HPCL, $\langle N_{AB_2} \rangle$, and (2) size exclusion chromatography capable of a multiangle laser light scattering (SEC-MALLS); the latter was also compared with a conventional SEC results. The absolute numberaverage molecular weights, M_n 's of HPCLs both from (1) and (2) were reasonably coincident in the range between ca. 11 000 and 15 000.

3. Small-angle X-ray scattering (SAXS) enabled to estimate the radii of gyration, $R_{\rm g}$, of HPCLs and LPCL, particularly by curve fits of the Zimm plot represented as 1/I(q) vs q^2 with the Zimm scattering function. Then, the branching ratio, g, of the mean-square value of R_{g} for HPCL to that for LPCL was used to characterize the relative degree of branching (DB) of HPCLs relative to LPCL. The DBs of HPCLs were found to be considerably influenced by the length of the linear $olig(\epsilon$ -caprolactone) segments repeated in the backbone chains; the shorter the olig(ϵ -caprolactone) segments, the higher the DB in the order HPCL-5 > HPCL-10 > HPCL-20. Also found were the presence of any correlative effect of DB on the thermal transition and degradation. The melting transitions of HPCLs were elevated in accordance with decrease in the number of $oligo(\epsilon$ -caprolactone) segments and hence increase in the degree of branching, while vice versa for the thermal degradation.

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