Synthesis and Characterization of a Series of Star-Branched Poly(ε-caprolactone)s with Nanoscale Molecular Architectural Variation

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ABSTRACT

A series of star-branched poly(ε-caprolactone)s (SPCLs) was synthesized with nanoscale molecular architectural variation in arm numbers and lengths by ring-opening polymerization under bulk condition. Arm numbers were varied to be 3, 4, and 6 by the use of multifunctional initiating cores while arm lengths were varied by controlling molar ratio of monomer-to-initiating hydroxyl group molar ratio. Molecular weights were determined by both ^{1}H NMR end-group analysis and MALDI-TOF mass spectrometry. The branching architecture of SPCLs was evaluated by the branching ratio, g, which is the ratio of the mean-square radius of SPCL to that of liner counterpart, linear poly(ε-caprolactone) (LPCL). The radii of gyration of SPCLs and LPCLs were determined using small-angle X-ray scattering (SAXS) from the initial slopes of Zimm plots. Branching ratios as well as thermal properties and crystallinity were found to be also dependent on structural variations.

Keywords: star-branched polymer, poly(ε-caprolactone), branching ratio, thermal property, crystallinity

1 INTRODUCTION

Macromolecules with complex molecular architectures have drawn great attention among many scientists and engineers in relations to the functional materials for nanoscale application as new and/or improved material properties can be achieved by altering their specific molecular architecture.[1] One such example in this context is the dendritic macromolecules, which are largely classified into dendrimers, hyperbranched, and star-branched polymers.[2] Star-branched polymers, which can be distinguished by the structure containing several linear arms of similar molecular weight that emanate from a central core, represent a special case of branched polymers. Like dendrimers, they can possess a globular architecture and defined inner and peripheral groups, which imparts unique properties to the molecules.[3] At the same time, similarly to hyperbranched polymers, their synthesis can be accomplished expeditiously, which makes them promising candidates for practical application.[4] Moreover, owing to the progress in controlled polymerization techniques, star-branched polymers can be easily prepared with narrow molecular weight distribution and with predictable lengths and numbers of arms under modest condition.[5]

Recently, the ring-opening polymerization (ROP) methods have been increasingly adopted for preparing dendritic macromolecules with well-defined building blocks, controlled molecular weights, and narrow molecular weight distributions. Hedrick et al. developed a novel synthetic approach to hyperbranched as well as dendrimer-like star-branched aliphatic polyesters with a range of molecular architectural variation such as different lengths of linear backbone segments in each building block, the size of macromolecules, and the total molecular weights by means of ROP of ε-caprolactone.[6] However, the architectural characteristics as well as the correlation between architecture and properties of these hyper- and/or star-branched poly(ε-caprolactone)s have been much less pervasive than other types of dendritic macromolecules. Moreover, previous researches had focused mostly on synthetic variation of the composition of building blocks.

In this paper, we will describe the syntheses of a series of star-branched poly(ε-caprolactone)s (SPCLs) possessing architectural variations on arm numbers and lengths by means of ROP of ε-caprolactone. Chemical structures of synthesized SPCLs were confirmed by both ^{1}H and ^{13}C NMR spectroscopy, and the absolute molecular weights were determined by end-group analysis and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry. The branching architectures were compared by the branching ratio estimated from the ratio of the mean-square radius of gyration of a given SPCL to that of its linear counterpart. Here, small-angle X-ray scattering (SAXS) was utilized for determining the radii of gyration. The thermal properties and the degree of crystallinity were evaluated using differential scanning calorimetry (DSC) and by performing a thermogravimetric analysis (TGA).

2 EXPERIMENTAL

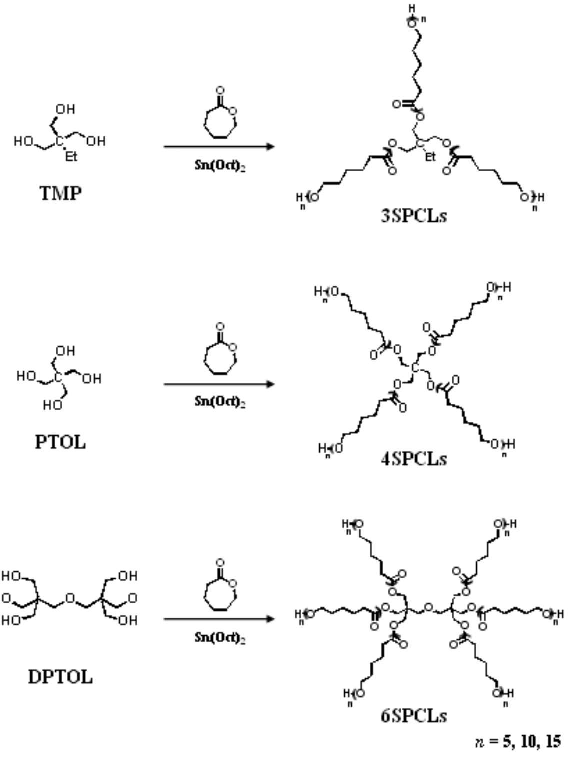
2.1 Synthesis

Star-branched poly(ε-caprolactone)s (SPCLs) were prepared by ring-opening polymerization of ε-caprolactone (CL, Aldrich) which was initiated with multifunctional initiating cores in the presence of catalytic amount of tin

(II) 2-ethylhexanoate, $Sn(Oct)_2$. Variation in the number of arms was accomplished by using different initiating core molecules having 3 (trimethylol propane, TMP), 4 (pentaerythritol, PTO), and 6 (dipentaerythritol, DPTOL) hydroxyl groups (Scheme 1). On the other hand, the arm lengths were varied by controlling monomer-to-hydroxyl group molar ratio, which was $[CL]_0/[–OH]_0 = 5$, 10, and 15. The average degrees of polymerization of CL onto each hydroxyl group, *n* in Scheme 1, were found to be perfectly controlled by this method. The basic reaction procedure of the SPCLs is as follows. 500 mmol of CL and a certain amount of multifunctional core were put into the reaction flask, which was followed by the three repeated session of evacuation and argon purging processes. The flask was then immersed into an oil bath stabilized at 110 °C with vigorous stirring to form a homogeneous mixture, to which the catalytic amount of $Sn(Oct)_2$ was added. The evacuating and argon purging processes was repeated again and the polymerization was allowed to proceed under dry argon atmosphere for 24 h. On the basis of the different arm numbers (*m*) and arm lengths (*n*), the resulting SPCLs of the present study were accordingly designated as *m*SPCL–*n* where $m = 3, 4, 6$, and $n = 5, 10, 15$, respectively.

Linear poly(ε-caprolactone)s (LPCLs) were prepared by the same procedure as that of the SPCLs, except that EtOH which was used as an initiator and $[CL]_0/[–OH]_0$ was varied to be 17, 32, 42, and 63, respectively, in order to control the molecular weights of the resulting LPCLs.

Scheme 1: Synthesis of star-branched poly(ε-caprolactone)s



2.2 Characterization

Chemical structures of synthesized SPCLs as well as LPCLs were characterized via ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy. Both ^1H and ^{13}C NMR spectra were acquired on a Bruker Avance DPX–300 (300 MHz for ^1H and 75 MHz for ^{13}C) spectrometer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as an internal standard. Matrix-assisted laser desorption/ ionization time-of-flight (MALDI-TOF) mass spectrometric measurements carried out on a PerSeptive Biosystems-Voyager-DE STR spectrometer equipped with a nitrogen laser (337 nm, 3 ns pulse width) in deflected mode. The accelerating voltage was fixed at 20 kV, the grid voltage 80 %, and the guide wire voltage 0.1 %. The radii of gyration, R_g's, of the SPCLs and their linear counterparts, LPCLs, were determined by small-angle X-ray scattering (SAXS). The SAXS intensity distribution, $I(q)$, was measured as a function of scattering vector, q, with a rotating-anode X-ray generator (Bruker AXS Nanostar) operated at 40 kV and 35 mA, of which X-ray source was a monochromatized CuKα ($\lambda = 1.54$ Å) radiation. Melting temperature, T_m, and the heat of fusion, ΔH_m, for the SPCLs were measured by differential scanning calorimetry (DSC) with a TA Instruments DSC 2920 at a heating rate of 20 °C/min under a nitrogen atmosphere. Thermogravimetric analysis (TGA) was carried out on a TA Instruments TGA 2050 thermal analyzer at a heating rate of 20 °C/min under a nitrogen atmosphere and the masses of samples were approximately 5-10 mg.

3 RESULTS AND DISCUSSION

3.1 Synthesis of SPCLs

Synthetic routes to the star-branched poly(ε-caprolactone)s (SPCLs) with the variation in both arm numbers and lengths are well represented in Scheme 1. The arm number variation was realized by using different multifunctional cores having 3, 4, and 6 hydroxyl groups which were TMP, PTOL, and DPTOL, respectively. ROP of CL with variable molar ratios of CL-to-initiation hydroxyl group in multifunctional cores ($[CL]_0/[–OH]_0 = 5$, 10, and 15) enabled a controlled variation of arm length of the resulting SPCLs. Table 1 summarizes the conditions for preparing SPCLs and LPCLs. The chemical structures of the resulting SPCLs were confirmed from both ^1H NMR and ^{13}C NMR spectra. In addition, ^1H NMR spectra of SPCLs and LPCLs were also analyzed to determine the average degree of polymerization of arm segments of SPCLs, $\langle DP_{CL} \rangle$, and the number-average molecular weights, $M_{n,NMR}$. In ^1H NMR spectra of SPCLs, the peak assigned to the chain ends ($–CH_2OH$, δ 3.65) and the peak assigned to the repeating methylene units ($–COCH_2$, δ 2.31) in poly(ε-caprolactone) segments were quite distinguishable, therefore, the $\langle DP_{CL} \rangle$ values could be easily calculated from the ratios of the integrated area of these peaks.

sample	Initiator entry	Number of OH	$[\text{CL}]_0$ $/[\text{–OH}]_0$	1H NMR		MALDI-TOF		DSC		DSC
				$<DP_{\text{CL}}>$	$M_{\text{n,NMR}}$	$M_{\text{n,MALDI}}$	M_w/M_n	T_m (°C)	X_c (%)	T_{d10} (°C)
3SPCL–5	TMP	3	5	5.6	2,100	2,000	1.08	37.9	52.9	319
3SPCL–10	TMP	3	10	10.4	3,700	3,600	1.17	45.5	54.6	322
3SPCL–15	TMP	3	15	15.4	5,400	5,300	1.22	50.2	56.1	326
4SPCL–5	PTOL	4	5	5.5	2,800	2,800	1.09	40.0	52.2	320
4SPCL–10	PTOL	4	10	10.6	5,100	5,100	1.17	45.7	54.1	323
4SPCL–15	PTOL	4	15	15.5	7,400	7,200	1.18	50.5	55.5	326
6SPCL–5	DPTOL	6	5	5.3	3,900	3,800	1.12	40.7	50.5	320
6SPCL–10	DPTOL	6	10	10.4	7,400	7,400	1.17	45.3	53.6	322
6SPCL–15	DPTOL	6	15	15.2	10,700	N/A	N/A	51.2	55.1	327

Table 1: Synthetic conditions and general characteristics for SPCLs and LPCLs.

As listed in Table 1, the calculated $<DP_{\text{CL}}>$ values for SPCLs as well as those for LPCLs were found to be in good agreement with those of the targeted values, which are solely predictable from the $[\text{CL}]_0/[\text{–OH}]_0$ ratios. The number-average molecular weights of the SPCLs and LPCLs, $M_{\text{n,NMR}}$, were calculated from the following equation (See Table 1):

$$M_{\text{n,NMR}} = MW_{\text{Ini}} + MW_{\text{CL}} \times \left\langle DP_{\text{CL}} \right\rangle \tag{1}$$

where MW_{Ini} is the molecular weight of initiating species and MW_{CL} is that of CL.

Figure 1 depicts the MALDI-TOF mass spectra for 4SPCLs. The mass difference between each adjacent peak, Δm, is 114 Da, which corresponds well with the mass of the CL repeating unit of the chain segments in SPCLs. Arm length variations made by controlled increase in the $[\text{CL}]_0/[\text{–OH}]_0$ shifted the whole mass distribution curves to higher molecular weights while the distribution shape showed no significant changes. The $M_{\text{n,MALDI}}$ and molecular weight distributions for SPCLs were derived from the mass spectra and listed in Table 1. For the SPCLs, $M_{\text{n,MALDI}}$ was found to be in good agreement with $M_{\text{n,NMR}}$.

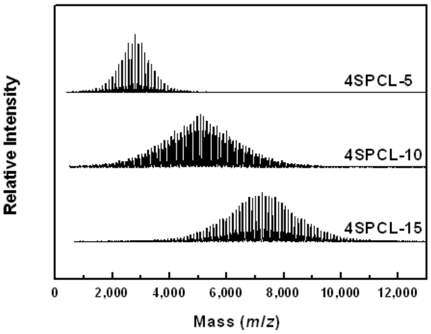


Figure 1: MALDI-TOF mass spectra of 4SPCLs.

3.2 Branching Ratio

In order to characterize the effect of the branching architecture on molecular dimension, the branching ratio, g, was estimated from the ratio of the mean-square radii of gyration between a given star-branched molecule and its linear counterpart with the same chemistry and similar molecular weight as follows:[7]

$$g = \frac{< R_g{}^2 >_{\text{branched}}}{< R_g{}^2 >_{\text{linear}}} \tag{2}$$

where $<R_g{}^2>_{\text{branched}}$ and $<R_g{}^2>_{\text{branched}}$ denote the mean-square radius of gyration of star-branched molecule and that of linear counterpart, respectively. It should be noted that the parameter g is always < 1, and decreases with increase in degree of branching, because branched molecules occupy less volume in solution than linear polymers of the same molecular weight. The radii of gyration for SPCLs as well as those for their linear counterpart were determined by small-angle X-ray scattering (SAXS). Assuming that solutions are very dilute and in a non-interacting system, the scattering curves obtained from polymer solutions can be simplified as a function of only model particle scattering function, $P(R_g,q)$, which enables us to extract the R_g values from the scattering curves by performing a weighted nonlinear, least-square that fit the scattering curves over the q range, $[q_{\min}, q_{\max}]$:[8]

$$I(q) = A \times P(R_g, q) + B, \; \left[q_{\min}, q_{\max}\right] \tag{3}$$

The most common model particle scattering function is one suggested by Zimm[7] which is shown below:

$$P_{\text{Zimm}}(R_g, q) = 1 \Big/ \left(1 + \frac{q^2 R_g{}^2}{3}\right) \tag{4}$$

Figure 2 shows the typical scattering curves for the SPCLs observed by SAXS. It should be noted that Zimm plot of 6SPCL–10 appeared linear over a relatively large q range.

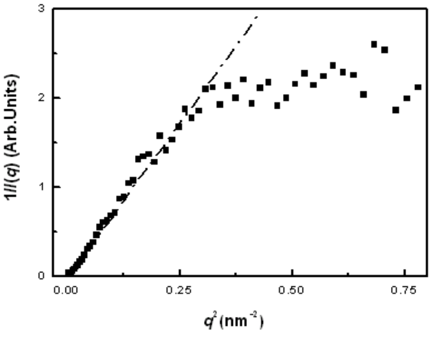


Figure 2: Zimm plot for 6SPCL–10.

In order to elucidate the effects of arm numbers and lengths on molecular dimension, the R_g values for 4SPCLs, SPCL–10's, and their counterparts were determined.

As illustrated in Figure 3, for the SPCLs with the same arm number, the *g* values remained almost constant (*g* = ca.0.8). This indicates that the segment density was not significantly varied when the arm length was increased. However, the *g* values were observed to decrease for SPCLs with increasing arm number having a constant arm length being constant. This indicates that more branching points resulted in more compactly packed volume in the solution.

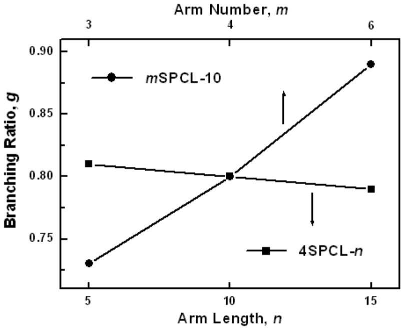


Figure 3: Dependence of *g* on arm lengths and numbers.

3.3 Thermal Properties

Thermal properties of SPCLs were characterized using both DSC and TGA. As listed in Table 1, the melting temperatures, T_m, for SPCLs of the same arm numbers are found to be fairly affected by arm length variation, which is assumed to be due to the presence of longer linear chains possibly facilitating the ordered chain packing to crystallize more efficiently.[9] The degree of crystallinity, X_c, of SPCLs were calculated as follows:

$$X_c(\%) = \frac{\Delta H_m}{\Delta H_m{}^0} \times 100 \qquad (5)$$

where ΔH_m is the apparent enthalpy of melting and $\Delta H_m{}^0$ is the extrapolated value of enthalpy corresponding to the melting of a 100% crystalline poly(ε-caprolactone), which was previously reported as 136.4 J/g.[10] As listed in Table 1, the X_c for SPCLs of the same arm number was increased with increasing arm length. However, the X_c for SPCLs of the same arm length was only minimal with increased arm numbers, which is regarded to be due to the competing effects of increased molecular weight and branching.

Thermal degradation stability of the SPCLs was evaluated using the temperature of 10% weight loss of the polymers, T_{d10}. As indicated in Table 1, the T_{d10} of 4SPCLs are seen to shift toward a higher temperature region as the arm length was increased. Considering that thermal degradation of poly(ε-caprolactone) involves an unzipping depolymerization from the hydroxyl end of the polymer chain.[11] increase in T_{d10} of SPCLs with longer arms are believed to be attributed to the lower number of polymer chain ends. On the contrary, T_{d10} for SPCLs of similar molecular weight were found to decrease as arm numbers increased, which may result in the higher number of chain ends and consequently resulting in the acceleration of unzipping degradation.

4 CONCLUSIONS

A series of star-branched poly(ε-caprolactone)s (SPCLs) was successfully synthesized with structural variation of arm numbers and length. Structural variations among SPCLs were verified to be precisely controlled as evidenced by ^{1}H and ^{13}C NMR spectra. The absolute values of molecular weight were obtained by both ^{1}H NMR end-group analysis and MALDI-TOF mass spectrometry, of which results were reasonably consistent. The molecular dimension of SPCLs was estimated using the radius of gyration, R_g, determined by SAXS curve fits to the Zimm scattering function. The branching ratio, *g*, was calculated from the ratio of the mean-square radius of gyration of each SPCL to that of its linear counterpart. In addition, *g* was observed to be fairly affected by arm number variation; the higher arm numbers, the smaller *g* values, and thus more compact molecular structure in order of 3SPCL–10 > 4SPCL–10 > 6SPCL–10, while the effect of arm length variation on g of SPCLs was found to be only minimal. We also found the correlative effect of structural variation on the thermal transitions as well as the degree of crystallinity. The T_m was found to increase with increasing arm length. Similarly, the T_{d10} was observed to be an increasing function of arm length. On the contrary, we did not observe any significant changes in both the T_m and T_{d10} for the SPCLs of the same arm length but with arm number variation. However, for the SPCLs of the equivalent molecular weight, the degree of crystallinity was found to decrease with increasing arm numbers.

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