Synthesis of Ultra-Small Branched Star Poly(e-caprolactone)s and their High End Group Concentration Effects on Crystallization

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ABSTRACT: We successfully synthesize the three- and six-branched star poly(e-caprolactone)s with extremely small branched segments (USB-SPCLs) using a facile pseudo-one-pot process in a pilot scale and investigate the effect of ultra-small branches on their crystallization behaviors. The number of branched segments and the individual branched segment lengths for USB-SPCLs are precisely controlled via manipulating monomer-to-core ratio, adjusting monomer-to-polymer conversion, end-capping the terminal hydroxyl groups, and vacuum purification, which results in USB-SPCLs having the branched segments below five degree of polymerization with a high yield exceeding 93%. The molecular weights obtained from 1H NMR spectroscopy are consistent with that obtained from MALDI-TOF-MS and the molecular weight distributions are narrow with $M_w/M_n \leq 1.2$, indicating that USB-SPCLs have mono-dispersed branches. USB-SPCLs have low melting temperatures and broad double-melting peaks attributed to their extremely small branches, and the crystallization behaviors for USB-SPCLs depend on the end group concentration. On the other hand, the glass transitions for USB-SPCLs depend on the total molecular weights, regardless of the number and length of branched segments. © 2015 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. 2015, 53, 1134–1142

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INTRODUCTION Poly(e-caprolactone)s (PCLs), which have been studied extensively over the past 20 years, are one of the most attractive biocompatible and biodegradable polymers.1–8 PCLs low glass transition temperature, low melting temperature, and high miscibility with commercial polymers compared with other polymers provide significant advantages to the use of PCLs in absorbable sutures, surgical fibers, artificial organs, controlled drug delivery applications, tissue regeneration approaches, food packages, and PVC plasticizers.2–11 PCLs are produced via the ring-opening polymerization (ROP) of the cyclic ester monomer, e-caprolactone (CL). The mechanism by which CL undergoes ROP in the presence of an alcohol initiator and a catalyst is well known.12,13 The alcohol initiator combines with the catalyst to form a complex that rapidly reaches equilibrium, and the complex initiates and propagates the polymerization of the CL monomer via a classical coordination-insertion mechanism. This ROP mechanism enables PCLs to polymerize to form a variety of well-controlled architectures, with variations in the number and length of branched segments, depending on the number of hydroxyl groups in the initiator and the molar ratio between the CL monomer and the initiator hydroxyl groups.3,9 Additionally, the molecular weight distribution (MWD) of PCLs product is narrow. Thus, the ROP of the CL monomer is regarded to as a sort of living polymerization.14

Star poly(e-caprolactone)s (SPLCs) are the simplest branched polymers consisting of several PCL branches that emanate from a central core.15–18 The branches of SPLCs provide a smaller hydrodynamic radius and a greater number of end groups than are obtained from linear PCLs (LPCLs), and SPLCs exhibit useful properties that are not available to conventional LPCLs, such as a low melting point,15 a low crystallinity,16 a rapid molecular motion,16 a low melt viscosity,16 a low glass transition temperature,19 a low degree of entanglement in the solid state,20 and a high solubility in various solvents.21 In particular, SPLCs provide fundamental insight into structure–property relationships of various and complicated branched polymers, such as H-shaped, comb-shaped, or pom-pom-shaped polymers, due to their simple branched structure and living polymerizable property. However, most

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studies of SPCLs have been carried out with large branched segments, and few studies have examined SPCLs with extremely small branches having an average length of fewer than five CL repeating units, that is, a degree of polymerization (DP) ≤ 5. This is attributed to the backbiting transesterification side reactions that occur during the CL polymerization.22–26 Such inter- and intramolecular transesterification side reactions of SPCLs proceed via nucleophilic attack of the terminal hydroxyl groups on the ester carbonyl groups in their branched segments, resulting in the collapse of desired SPCL structure and the formation of undesirable cyclic PCLs, and hence a low yield was observed.22–26 These side reactions tend to proceed readily among SPCLs with small branched segment lengths due to the high end group concentrations and occur rapidly as the monomer-to-polymer conversion approaches completion.9,22 For this reason, the precise synthesis of SPCLs with extremely small branches is not as easy as we think it will be, although they have highly attractive advantages, including high biocompatibility, facile control over degradation, low softening and melting points, low crystallinity, and good miscibility with other materials compared with conventional SPCLs.1,27 Recently, Shibita et al. reported the synthesis of tetra-armed SPCL with extremely small branches to use as semi-interpenetrating polymer networks.28–30 Tetra-armed SPCL appeared to be successfully synthesized, but it had a low yield (76%). Bilgin and Yaçi reported the synthesis and characterization of octa-armed SPCL with extremely small branches.31 They showed that octa-armed SPCL had very low yield (56%) and higher molecular weight compared with the targeted molecular weight. These results are attributed to the synthesis carrying out without consideration of the chronic backbiting problem associated with PCLs. In those studies, the desired SPCL structure may collapse, and/or the undesirable cyclic PCLs may form. Actually, we overcame the backbiting problem and successfully investigated the use of well-defined SPCL with extremely small branches as a non-toxic PVC plasticizer. The phthalate-free flexible PVC plasticized by the SPCL had a good processability, an excellent stretchability, and a migration resistance, but nevertheless the main synthetic factors and detailed synthetic results for well-defined SPCL with extremely small branches were not discussed in our previous publication.32

Herein, we demonstrated the facile synthesis of ultra-small branched SPCLs (USB-SPCLs) with precisely controlled architectures using a pilot-scale pseudo-one-pot process via manipulating monomer-to-core ratio, adjusting monomer-to-polymer conversion, end-capping the terminal hydroxyl groups, and vacuum purification. This synthetic protocol did not permit backbiting transesterification side reactions, thereby enabling us to easily control the molecular architectures of SPCLs, even with extremely small branched segments, and to obtain high-purity USB-SPCLs with a high yield. Additionally, this synthetic procedure was green and straightforward, in that organic solvents and additional processes (e.g., precipitation, filtering, washing, and drying steps) were not needed. We further described that USB-SPCLs exhibit the reduced crystallization and the total molecular weight-dependent glass transition attributed to their extremely small branches. This study paves the way for the development of various and complicated PCLs with extremely small branched segments and for an understanding of the structure–property relationships affected by their extremely small branches.

**EXPERIMENTAL**

**Materials**

ε-Caprolactone (CL) and trimethylolpropane (TMP) were purchased from Alfa Aesar Co., Ltd., USA and Tokyo Chemical Industry Co., Ltd., Japan, respectively. Dipentaerythritol (DPTOL), tin(II) 2-ethylhexanoate (Sn(Oct)2), and acetic anhydride (Ac2O) were purchased from Sigma-Aldrich Ltd., Korea. TMP and DPTOL were dried under vacuum at room temperature for 24 h before use, and other chemicals were used without further purification.

**Synthesis of USB-SPCLs**

The synthesis of ultra-small branched SPCLs (USB-SPCLs) was accomplished by the ROP of the CL monomer through a facile pseudo-one-pot bulk process without organic solvents. The calculated quantity of core material was added to a 1 L pilot-scale reactor in the presence of 570.70 g (5.00 mol) of the CL branching material, and the mixture was stirred vigorously with heating to form a homogeneous mixture over 1 h. After then, the mixture was heated in an oil bath at 110 °C, and a catalytic amount of Sn(Oct)2 was added. After polymerization for about 3 h, an excess quantity of the Ac2O end-capping agent was added, and the reaction was allowed to proceed at 110 °C for 30 min to terminate the polymerization reaction by capping the terminal hydroxyl groups of the as-polymerized USB-SPCLs. The residual unreacted CL monomers and excess Ac2O were removed under vacuum at 110 °C over 24 h, yielding end-capped USB-SPCLs with small acetate end groups (>93% of yield). The number of branched segments in USB-SPCLs was controlled by initiating core moieties having either three (TMP) or six (DPTOL) hydroxyl functionalities. The length of the individual branched segments of USB-SPCLs, that is, the degree of polymerization (DP) of the individual branched segments, was varied by manipulating the molar ratio between the CL monomer and the hydroxyl functionalities of the core moiety ([CL]/[core-OH]). The number of branched segments (n) and the DP of the individual branched segments (n) of USB-SPCLs were varied to prepare four USB-SPCLs, denoted USB-SPCLm-n: USB-SPCL3-3, USB-SPCL3-5, USB-SPCL6-3, and USB-SPCL6-5. As a counterpart to USB-SPCLs, the conventional LPCL and SPCL were synthesized from ethanol and TMP core, respectively, using procedure used for the production of USB-SPCL. These conventional LPCL and SPCL had individual branched segment lengths of DP = 10 and were denoted LPCL1-10 and SPCL3-10, respectively. LPCL1-10 had a total molecular weight similar to that of USB-SPCL3-3, and SPCL3-10 had longer branched segment lengths but the
same number of branched segments as USB-SPCL3-3. All reactions were performed under a nitrogen atmosphere with the exception of the vacuum purification.

Characterization
Fourier-transform infrared (FT-IR) spectroscopy was employed to characterize the functional groups present in USB-SPCLs using a Perkin-Elmer GX IR spectrophotometer with a spectral resolution of 4 cm⁻¹. The FT-IR spectrum was collected over the range 4000 to 400 cm⁻¹ using potassium bromide (KBr) powder as the sample matrix and reference material. The chemical structures of USB-SPCLs were analyzed by ¹H nuclear magnetic resonance (NMR) spectroscopy using a Bruker Avance spectrometer 600 using chloroform-d (CDCl₃) as the solvent. The molecular weights of USB-SPCLs were measured by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) using an Applied Biosystems Voyager-DE STR spectrometer and a matrix comprising di-hydrobenzoic acid (DHB) dissolved in tetrahydrofuran (THF). The melting, crystallization, and glass transition behaviors of USB-SPCLs were measured by differential scanning calorimetry (DSC) using a Netzsch DSC 200 F3. Samples were heated to 140 °C at a heating rate of 20 °C min⁻¹ and were cooled to −110 °C at a cooling rate of −5 °C min⁻¹. The samples were then reheated to 140 °C at a heating rate of 20 °C min⁻¹ under a nitrogen atmosphere.

RESULTS AND DISCUSSION
Synthesis of USB-SPCLs
We synthesized end-capped three- or six-branched SPCLs with individual branched segment lengths of DP ≤ 5, that is, ultra-small branched SPCLs (USB-SPCLs). As shown in Figure 1(a), the FT-IR spectra of USB-SPCLs revealed that the ester C=O stretch absorbance peak at 1730 cm⁻¹ shifted to 1735 cm⁻¹ after the ROP of the CL monomer from the core materials. Furthermore, the outstanding O–H stretch (3650–3200 cm⁻¹) observed in both core materials disappeared completely, and a weak overtone band resulting from the ester groups in USB-SPCLs appeared at 3700–3300 cm⁻¹. These results indicated that the ROP successfully proceeded without leaving any CL monomers, that the PCL branched segments were successfully grown from a core moiety, and that the terminal hydroxyl groups of USB-SPCLs were completely capped with small acetate groups. A more precise architectural analysis of USB-SPCLs was performed using ¹H NMR spectroscopy. As shown in Figure 1(b), the ¹H NMR spectra of USB-SPCLs showed peaks typically observed in conventional PCLs, including the core moiety peaks (0.89 ppm for TMP or 3.39 ppm for DPTOL) and the end-capped acetate peak (2.04 ppm). On the contrary, the CL monomer peaks (4.22, 2.63, 1.86, and 1.76 ppm) were completely absent, and the methylene proton peak adjacent to the terminal hydroxyl groups (3.64 ppm) and the hydroxyl proton peak (3.41 ppm) observed in the as-polymerized uncapped USB-SPCLs were also disappeared. These indicated that the synthesis of end-capped USB-SPCLs was successfully accomplished without leftover CL monomers, in good agreement with the FT-IR analysis. The ratios of the integrals of specific ¹H NMR peaks obtained from USB-SPCLs identified the number of branched segments, \( N_{\text{number}} \), and the average lengths of the individual branched segments, \( N_{\text{length}} \), of USB-SPCLs (see ¹H NMR spectra with the integration values in Supporting Information, Fig. S1). The \( N_{\text{number}} \) values of USB-SPCLs were calculated from the ratio between the integrals of peak corresponding to the methyl protons (g, 0.89 ppm, \(-\text{CH}_3\text{CH}_3\) in TMP) or methylene protons (g', 3.39 ppm, \(-\text{OCH}_2\text{CH}_3\) in DPTOL) in the core moiety and the peak corresponding to the methyl protons of the end-capped acetate groups (e, 2.04 ppm, \(-\text{COCH}_3\)). As listed in Table 1, the \( N_{\text{number}} \) values corresponded to the number of branched segments and the average lengths of the individual branched segments. Figure 1(c) shows the MALDI-TOF mass spectra of USB-SPCLs. These indicate that the synthesis of end-capped USB-SPCLs was successfully accomplished without leftover CL monomers, in good agreement with the FT-IR analysis.
number of hydroxyl groups in the core materials, indicating that the TMP- and DPTOL-cored SPCLs included three- and six-branched segments, respectively. The $N_{\text{length}}$ values of USB-SPCLs were calculated by counting the number of CL repeating units, that is, the degree of polymerization (DP), in one branched segment of USB-SPCLs based on the ratio of the peak integrals corresponding to the methyl protons of the end-capped acetate groups ($e$, 2.04 ppm, $-\text{COCH}_3$) and the repeating methylene protons adjacent to the carboxyl groups in the branched segments ($a$, 2.31 ppm, $-\text{COCH}_2\text{CH}_2$-). As listed in Table 1, USB-SPCLs were obtained with the desired individual branched segment lengths of three (DP = 3) or five (DP = 5) CL repeating units, depending on the molar ratio of the CL to the hydroxyl groups on the core material ([CL]/[core-OH]). These results indicated that the molecular architecture of USB-SPCLs was precisely controlled with below 5 nm branched segment lengths in a fully extended conformation.

The number-average molecular weights of USB-SPCLs were determined using $N_{\text{number}}$ and $N_{\text{length}}$ obtained from the $^1$H NMR spectra, as follows:

$$M_{n,\text{NMR}} = \frac{\text{MW}_{\text{core}} + (\text{MW}_{\text{CL}} \times N_{\text{length}} \times N_{\text{number}})}{N_{\text{number}}} + (\text{MW}_{\text{end-cap}} \times N_{\text{number}}) - (\text{MW}_{\text{Na}} \times N_{\text{number}})$$

where $\text{MW}_{\text{core}}$, $\text{MW}_{\text{CL}}$, $\text{MW}_{\text{H}}$, and $\text{MW}_{\text{end-cap}}$ are the molar masses of the core material (TMP or DPTOL), CL monomer, hydrogen, and end-capping moiety ($-\text{COCH}_3$), respectively. As shown in Table 1, the calculated $M_{n,\text{NMR}}$ values of USB-SPCLs were close to the actual number-average molecular weights of USB-SPCLs, determined by MALDI-TOF-MS, $M_{n,\text{MALDI}}$. The MALDI-TOF mass spectra of USB-SPCLs in Figure 1(c) displayed that each mass peak corresponded to the molar mass of "$\text{MW}_{\text{core}} + (n \times \text{MW}_{\text{CL}}) + \text{MW}_{\text{end-moiety}} + \text{MW}_{\text{Na}}$" where $n$ is positive integer values, $\text{MW}_{\text{end-moiety}}$ is the molar mass of "$(\text{MW}_{\text{end-cap}} \times \text{MW}_{\text{H}}) \times 3$ (for TMP) or 5 (for DPTOL)" and $\text{MW}_{\text{Na}}$ is the molar mass of the sodium cation. The mass difference between each adjacent peak was 114 $m/z$ (mass-to-charge ratio), which corresponded to the molar mass of a CL repeating unit in branched segments. Moreover, an increase in the total molecular weights of USB-SPCLs shifted the entire MALDI-TOF mass spectrum toward higher molecular weights without significantly altering the shape of the spectrum. These results provided the evidence that USB-SPCLs with well-defined architecture were synthesized without the formation of the undesirable structure, especially cyclic PCLs via the backbiting transesterification side reaction. (MWDs) of USB-SPCLs were narrow ($M_w/M_n \leq 1.2$) and independent of $N_{\text{length}}$ for a given $N_{\text{number}}$ (see Table 1), in contrast with previous reports on the MWD of SPCLs with longer $N_{\text{length}}$.$^{16}$ Furthermore, the MWD values of USB-SPCLs decreased as $N_{\text{number}}$ increased for a given $N_{\text{length}}$. These results suggested that the MWDs of USB-SPCLs were affected not by $N_{\text{length}}$, but rather by $N_{\text{number}}$.

We note that adjusting monomer-to-polymer conversion and end-capping the terminal hydroxyl groups were crucial for the synthesis of USB-SPCLs with precisely controlled architectures. Figure 2 is the $^1$H NMR spectra of the as-polymerized uncapped USB-SPCL3-3 (before purification) at different reaction times for a given quantity of catalyst and reaction temperature. As shown in Figure 2, the peaks corresponding to the unreacted CL monomer reduced as the reaction time increased, and eventually disappeared over the reaction time of 3 h, indicating that CL monomers was fully converted to USB-SPCL3-3 over the reaction of 3 h. The quantitative monomer-to-polymer conversion efficiency was calculated based on the ratio of $^1$H NMR peak integrals corresponding to the methylene protons in the unreacted CL monomer and the branched segments of USB-SPCL3-3 (see $^1$H NMR spectra with the integration values in Supporting Information, Fig. S2). As expected, we found that the complexity and information content of the spectra increased with increasing the reaction time, indicating that the reaction proceeded with high efficiency.
monomer-to-polymer conversion efficiency over 99.9% was accomplished over the reaction time of 3 h. In addition, as CL monomers were converted to USB-SPCL3-3, that is, as the reaction time progressed, the $N_{\text{length}}$ values of USB-SPCL3-3 gradually increased. The targeted $N_{\text{length}}$ value (DP = 3) was observed in the 3 h sample with a 96% monomer-to-polymer conversion efficiency. On the other hand, the $N_{\text{length}}$ values exceeded the targeted value over the reaction time of 3 h, although there were no longer any CL monomers to react with USB-SPCL3-3. The excess $N_{\text{length}}$ values can be explained by the formation of undesired cyclic PCLs attributed to the backbiting transesterification side reaction because the cyclization of PCLs by the backbiting transesterification side reaction readily occurred during the ROP of the CL monomer as the monomer-to-polymer conversion approached completion.9,22 These results obviously showed that the control of the monomer-to-polymer conversion played an important role in the synthesis of USB-SPCLs with the mono-dispersed branches, in other words, the monomer-to-polymer conversion should be carefully controlled to synthesize USB-SPCLs with well-defined architecture through cooperatively tuning up the reaction conditions, such as quantity of catalyst, reaction temperature, and reaction time. The control of the monomer-to-polymer conversion to prevent the backbiting transesterification side reaction during the ROP of the CL monomer, however, has not been reported before in the literature for the synthesis of well-defined PCLs. Many researchers have carried out the ROP of the CL monomer with a rough amount of catalyst and reaction time without considering the monomer-to-polymer conversion, and such ROP can result in the failure of obtaining SPCLs with desired architectures, which may further lead to a lack of properties of SPCLs. Hence, we adjusted the monomer-to-polymer conversion of the as-polymerized uncapped USB-SPCLs to 95–97% in this study.

Since the resulting as-polymerized USB-SPCLs were transparent viscous liquids (or soft waxy) (see Fig. S3 in Supporting Information) and their solubilities were similar to that of the unreacted CL monomer, the precipitation and filtering methods commonly used to purify and collect typical PCLs were not available for USB-SPCLs. Other purifying and collecting techniques, such as extraction, chromatography, and centrifugation, were also inefficient or unavailable. Indeed, a similar purification problem exists in a commercially available SPCL comprising a TMP core and short branches (PCL-T). The $^1$H NMR and MALDI-TOF mass data obtained from PCL-T definitely revealed that the PCL-T contained many impurities and undesired structures, such as the unreacted TMP core materials, the unreacted CL monomers, and the cyclic PCLs corresponding to the molar mass of $n \times \text{MW}_{\text{CL}}$ (see Fig. S4 in Supporting Information). These results indirectly illustrated the difficulties associated with the production (including purification and collection) of SPCLs with extremely small branches. Thus, we used a vacuum evaporation technique with heating to purify the as-polymerized USB-SPCLs by eliminating unreacted CL monomers and to collect the purified USB-SPCLs in a high yield. As shown in Figure 3(a), the unreacted CL monomer peaks in the $^1$H NMR spectrum of the as-polymerized uncapped USB-SPCL3-3 before vacuum purification disappeared after vacuum purification, indicating the successful removal of unreacted CL monomers. The $N_{\text{length}}$ values, however, increased from 3.20 to 4.02 after vacuum purification of the as-polymerized uncapped USB-SPCL3-3 (see $^1$H NMR spectra with the integration values in Supporting Information, Fig. S5), indicating that an undesired reaction occurred in the as-polymerized USB-SPCL3-3 during the vacuum purification. The MALDI-TOF mass spectrum of the as-polymerized uncapped USB-SPCL3-3 before vacuum purification shown in Figure 3(b) displayed the targeted number-average molecular weight and narrow MWD. After
vacuum purification, however, the number-average molecular weight and MWD increased, and the undesired mass peaks corresponding to the cyclic PCLs were observed [Fig. 3(b)]. These results supported that the well-controlled structure of the uncapped USB-SPCL3-3 collapsed during the vacuum purification by the formation of undesired cyclic PCLs attributed to the backbiting transesterification side reaction. To solve the problems on the vacuum purification of the as-polymerized USB-SPCLs, we completely end-capped the terminal hydroxyl groups in the as-polymerized USB-SPCLs by small acetate groups. End-capping the branches of the as-polymerized USB-SPCLs resulted in the removal of unreacted CL monomers without inducing any changes in the molecular structure of USB-SPCLs during the vacuum purification because the terminal acetate groups inherently blocked the backbiting transesterification side reaction of USB-SPCLs. A schematic diagram of the reaction mechanism associated with the end-capping effects during the vacuum purification of USB-SPCLs is shown in Figure 4. Finally, we could synthesize molecularly well-defined three- and six-branched star PCLs with ultra-small branched segments (DP 3 or 5), as confirmed by FT-IR, 1H NMR, and MALDI-TOF mass measurements.

From a scientific and commercial perspective, our synthetic protocol via manipulating monomer-to-core ratio, adjusting monomer-to-polymer conversion, end-capping the terminal hydroxyl groups, and vacuum purification offers a promising method for the production of USB-SPCLs with a precisely controlled architecture and a high yield exceeding 93%. Furthermore, this method is straightforward (pilot-scale pseudo-one-pot process) and enables the accurate analysis and interpretation of the structure–property relationships in PCLs with extremely small branches.

**Crystallization Behaviors of USB-SPCLs**

The DSC 2nd heating thermograms of all USB-SPCLs exhibited broad double-melting peaks, as shown in Figure 5(a). The low-temperature endotherm of USB-SPCLs corresponded to the melting of the original crystals formed during the DSC first cooling process, and the high-temperature endotherm of USB-SPCLs resulted from the melting of the recrystallized crystals formed during the DSC second heating process.33,34 The exotherm corresponding to the recrystallization of USB-SPCLs during the DSC second heating process was hidden under the double endotherm peaks.33,34 By contrast, LPCL1–10 (with a total molecular weight similar to that of USB-SPCL3-3) and SPCL3-10 (with the same number of branched segments as USB-SPCL3-3) exhibited sharp single-melting peak at higher temperature (≥45 °C), as shown in Figure 5(b). These results suggested that the extremely small branched segments hindered the molecular packing of USB-SPCLs. Moreover, the crystallization behaviors of USB-SPCLs appeared to depend on not the molecular weight and the number of branched segments, but the branched segment length. Choi et al. reported that the defects among free chain ends disrupted the orderly folding pattern of the crystals and reduced interchain cooperativity.35 Hence, the apparent end group concentrations of USB-SPCLs were calculated based on the number of branched segments per molecule divided by the number-average molecular weight.36 The end group concentration values increased with decreasing N_length and with increasing N_number, and the order was USB-SPCL3-5 (14.22 × 10⁻⁴) < USB-SPCL6-5 (16.62 × 10⁻⁴) < USB-SPCL3-3 (22.90 × 10⁻⁴) < USB-SPCL6-3 (24.29 × 10⁻⁴). The values obtained from LPCL1–10 and SPCL3–10, on the other hand, were 8.13 × 10⁻⁴ and 8.11 × 10⁻⁴, respectively. The end group concentration values for USB-SPCLs were quite higher than those for LPCL1–10 and SPCL3–10 because USB-SPCLs had extremely small branches. This result supported that low melting temperatures and broad double-melting peaks of USB-SPCLs were attributed to their high end group concentrations. Additionally, USB-SPCLs were thought to have low crystallizability, small crystal size, and broad crystal size distribution because their high end group concentrations disturbed the crystallization of USB-

**FIGURE 4** Schematic diagram showing the reaction mechanism associated with the end-capping effects during the vacuum purification of USB-SPCLs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
SPCLs due to a higher degree of hindrance in the chain ordering by increasing the end group concentration. Figure 5(c) revealed that the melting temperatures of USB-SPCLs at the maximum endotherm intensity were inversely proportional to the end group concentration values. In particular, USB-SPCL3-3 and USB-SPCL6-3, which had higher end group concentrations, showed lower melting temperatures than the others. Thus, USB-SPCL3-3 and USB-SPCL6-3 were liquids, even at room temperature (Supporting Information Fig. S3).

The effects of the extremely small branched architecture (with high end group concentration) on the ordered chain arrangement and packing of USB-SPCLs were explored in greater detail by analyzing the crystallization parameters. The crystallization parameters of USB-SPCLs were obtained from the crystallization exotherms during nonisothermal crystallization at a cooling rate of $-5^\circ C/min$ [Fig. 5(d)]. The crystallization parameters correspond to the maximum peak temperature, $T_p$, the temperature at the intercept between the tangents to the baseline and to the high-temperature side of the curve, $T_c$, the initial slope at the inflection point on the high-temperature side of the curve, $|S|$, and the peak width at half-height, $\Delta W$. A schematic diagram of these four crystallization parameters is shown in

FIGURE 5 (a) DSC thermograms of USB-SPCLs during the heating scan. (b) DSC thermograms of LPCL1-10, SPCL3-10, and USB-SPCL3-3 during the heating scan. (c) The maximum endotherm temperature values of USB-SPCLs as a function of the end group concentration. (d) DSC thermograms of USB-SPCLs during the cooling scan. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
the inset in Figure 5(d). The other crystallization parameters were the enthalpy of crystallization, ΔHc, and the degree of crystallinity, Xc. All crystallization parameters of USB-SPCLs are listed in Table 2, including the Tc–Tp values. The Tp, Tc, |S|, ΔHc, and Xc values of USB-SPCLs decreased with increasing end group concentration, whereas the Tc–Tp and ΔW values of USB-SPCLs increased with increasing end group concentration. These results indicated that USB-SPCLs with higher end group concentrations had a slow rate of nucleation (low |S| value), and the nuclei were created over a wider temperature range. The slow rate of nucleation led to a low overall rate of crystallization (high Tc–Tp value) and a broad crystallite size distribution (high ΔW value), resulting in a small degree of crystallinity (low Xc). Thus, USB-SPCL6-3 with the highest end group concentration showed the smallest degree of crystallinity (28.2%) among USB-SPCLs, and the crystallization exotherm obtained from USB-SPCL6-3 was extraordinarily broad and low compared with those obtained from other USB-SPCLs, as shown in Figure 5(d). These crystallization behaviors agreed well with the melting behaviors of USB-SPCLs. On the other hand, the order of the glass transition temperature, Tg, values for USB-SPCLs was USB-SPCL3-3 < USB-SPCL3-5 ≈ USB-SPCL6-3 < USB-SPCL6-5, in disagreement with the order of their end group concentrations [Fig. 5(a) and Table 2]. The Tg values of USB-SPCLs interestingly were proportional to the total molecular weights, regardless of the molecular architecture, such as the number and length of branched segments. Such Tg values of USB-SPCLs appeared to result from their extremely small branches. We are investigating these unique behaviors in detail using dynamic analysis techniques, which will be dealt in our next publications.

CONCLUSIONS

This study provided a facile synthesis of ultra-small branched star poly(c-caprolactone)s (USB-SPCLs) using a pilot-scale pseudo-one-pot process. We showed that the monomer-to-core ratio, the monomer-to-polymer conversion, end-capping the terminal hydroxyl groups and vacuum purification should be significantly considered in order to synthesize USB-SPCLs with the well-defined architecture. This synthetic method solved a chronic backbiting problem associated with PCLs and prevented the collapse of USB-SPCL structures during the synthesis and purification process, resulting in precisely controlled USB-SPCLs having mono-dispersed small branches with a high yield. USB-SPCLs were transparent viscous liquids (or soft waxy) even at room temperature, and had low melting temperatures, broad double-melting peaks, and low crystallizability due to the extremely small branches. We believe that the synthetic method introduced here will enable the synthesis of a variety of PCL architectures with extremely small branched segment lengths. This study opens up a route to the development of new types of PCLs with unique properties and to an understanding of the effects of extremely small branched segments on molecular behaviors.

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REFERENCES AND NOTES