Total-molecular-weight-dependent Rouse dynamic of ultra-small branched star poly(ε-caprolactone)s as a single coarse-grain unit

Woohyuk Choi a, Jae Woo Chung b, **, Seung-Yeop Kwak a, *

a Department of Materials Science and Engineering, Seoul National University, 599 Gwanak-ro, Gwanak-gu, Seoul, 151-744, Republic of Korea
b Department of Organic Materials and Fiber Engineering, Soongsil University, 369 Sangdo-ro, Dongjak-gu, Seoul, 156-743, Republic of Korea

A R T I C L E   I N F O
Article history:
Received 7 April 2015
Received in revised form 1 September 2015
Accepted 2 September 2015
Available online 9 September 2015

Keywords:
Molecular dynamics
Star poly(ε-caprolactone)
Ultra-small branches

A B S T R A C T
The extremely small branched effects on molecular dynamics are investigated using well-defined star poly(ε-caprolactone)s containing ultra-small branches (USB-SPCLs) as a model system. USB-SPCLs interestingly show total-molecular-weight-dependent glass transitions regardless of the molecular architecture parameters, such as the number and length of branches, whereas typical star polymers with polymeric large branches show the end-group-concentration-dependent glass transitions. The viscoelasticity of USB-SPCLs does not depend exponentially on the individual branched molecular weight, as observed in typical star polymers, and instead follows the modified Mark–Houwink power law and the Bueche-modified Rouse model for unentangled linear polymers. The flow activation energy and the longest Rouse relaxation time of USB-SPCLs show that the individual branches of USB-SPCL are dynamically equivalent and that a whole USB-SPCL molecule moves with a simple uni-motion. These results suggest that a whole USB-SPCL molecule presumably acts as a dynamically-equivalent single coarse-grain unit because of the extremely small branches on the scale of 20–40 atoms.

1. Introduction

Over past decades, branched polymers (i.e., polymers with more than two chain ends per molecule) have attracted significant attention in varied scientific and industrial fields due to their distinctive properties, including low melting point, low melt viscosity, and rapid molecular motion, that differ from those of linear polymers [1–5]. Among various branched polymers, star-shaped polymers (also known as ‘star polymers’) are the simplest branched polymers having only one central tie point, and the understanding of their dynamic properties can provide fundamental insight into the development and characterization of more complex branched polymers, such as hyperbranched, dendritic, H-shaped, comb-shaped, and pom–pom polymers [4–7]. Thus, these structure–property relationships have exhaustively been investigated, especially in comparison with linear polymers. Kraus et al. first reported that the increase in the viscosity of star polymers with molecular weight did not occur according to a power law, as observed in linear polymers, but instead occurred exponentially [8]. Quack et al. showed that the viscosity of star polymers did not depend on the total molecular weight but only on the molecular weights of individual branching segments [9]. Similar findings were made by Mykhaylyk et al., who observed that the zero-shear-rate viscosity of hydrogenated star polybutadienes was exponentially dependent on the molecular weights of the arms rather than on the total molecular weights of the stars [10]. Acebo et al. also reported that the viscosity of multiam star block copolymers (hyperbranched poly(ethyleneimine)-b-poly(ε-caprolactone)) increased exponentially as the arm length (or arm molecular weight) of the star block copolymer increased [11]. These phenomena were attributed to the fact that star polymers are not able to reptate as linear polymers because of their central tie point that suppresses the translational motion of the branched segments [12]. Instead, star polymers can relax by contour-length fluctuations of branched segments. This contour-length fluctuation allows the branched segments to retract some distance down the confining tube toward the central tie point and then explore a new path by extending back in another direction [12,13]. Since deep retractions of branched segments in star polymers are not favored entropically and are exponentially unlikely, thus the viscoelastic properties of star polymers depend exponentially on the molecular weights of individual branching segments [12,13]. These studies clearly showed that the dynamics of star...
polymers were determined by the individual branched length and the central tie point. However, most of these previous studies addressed the dynamic behaviors of star polymers with polymeric large branches. Star polymers with extremely small branches and their dynamic behaviors have not been studied sufficiently although star polymers with extremely small branches are highly attractive due to the ease of control over degradation, low softening point, and good miscibility with other materials, compared with typical star polymers [14–17]. Thus, from both the scientific and industrial point of view, the various investigations into dynamic phenomena in star polymers with extremely small branches are positively necessary to use these highly attractive advantages in an extremely small branched system.

Star poly(ε-caprolactone)s (SPCLs) can be synthesized with a narrow molecular weight distribution (MWD) and the target molecular architecture (e.g., degree of branching and branching length) by a simple ring-opening polymerization [18,19]. Moreover, SPCLs are highly biocompatible and biodegradable polyesters, and have thus been widely investigated for pharmacological, biomed- ical, agricultural, and environmental purposes [16,19–22]. Despite such advantageous properties of SPCLs, SPCLs with extremely small branches have hardly been studied owing to the failure to obtain well-controlled SPCLs. The chronic backbiting problem occurs when attempting to synthesize and purify SPCLs, which results in the collapse of the PCL structure and the formation of undesirable cyclic PCLs, and eventually makes impossible the synthesis and isolation of the well-controlled SPCLs. We have already overcome these synthetic problems via the manipulating monomer-to-core ratio, adjusting the monomer-to-polymer conversion, end-capping the terminal hydroxyl groups, and vacuum purification using a facile pseudo-one-pot process on a pilot scale, resulting in precisely controlled SPCLs with extremely small branches (degree of polymerization (DP) in an extremely small branch <5) [14,15]. Furthermore, since the terminal hydroxyl groups of our SPCLs are completely capped with small acetate groups, it is anticipated that the dynamic behaviors of extremely small branches in SPCLs can be investigated without hydrogen-bonding effects.

In this study, we investigated the effects of extremely small branches on the dynamic behavior of a star polymer using well-defined ultra-small-branched star poly(ε-caprolactone)s (USB-SPCLs) as a model system. The glass transition, viscoelasticity, flow activation energy, and longest Rouse relaxation time of USB-SPCLs interestingly depended on total molecular weight regardless of molecular architecture parameters, such as the number and length of branched segments. Moreover, these dynamic phenomena of USB-SPCLs followed the modified Mark–Houwink power law and the Bueche-modified Rouse model for unentangled linear polymers rather than traditional star polymer models that depend exponentially on the individual branched molecular weight. This suggests that a whole USB-SPCL molecule acts as a dynamically-equivalent single coarse-grain unit with one Rouse-segmental motion. These results broaden and deepen the understanding of the molecular dynamic behaviors of star polymers with extremely small branches, and further this enables new applications for star polymers as well as more complex branched polymers with unique dynamic properties.

2. Experimental

2.1. Materials

Ultra-small-branched star poly(ε-caprolactone)s (USB-SPCLs) were synthesized by ring-opening polymerization (ROP) of ε-caprolactone (CL) monomers via manipulating the monomer-to-core ratio, adjusting the monomer-to-polymer conversion, end-capping the terminal hydroxyl groups, and vacuum purification in a facile pseudo-one-pot bulk process without organic solvents [14,15]. Eight different USB-SPCLs were synthesized in which the number of branches, \( N_{\text{number}} \), and the average lengths of the individual branches (the average DP per branch), \( N_{\text{length}} \), were varied. These polymers are denoted as USB-SPCL \( N_{\text{number}} - N_{\text{length}} \), and the specific polymers treated here are named USB-SPCL3-2 (where \( N_{\text{number}} = 3 \) and \( N_{\text{length}} = 2 \)), USB-SPCL3-3 (where \( N_{\text{number}} = 3 \) and \( N_{\text{length}} = 3 \)), USB-SPCL3-4 (where \( N_{\text{number}} = 3 \) and \( N_{\text{length}} = 4 \)), USB-SPCL3-5 (\( N_{\text{number}} = 3 \) and \( N_{\text{length}} = 5 \)), USB-SPCL6-2 (\( N_{\text{number}} = 6 \) and \( N_{\text{length}} = 2 \)), USB-SPCL6-3 (\( N_{\text{number}} = 6 \) and \( N_{\text{length}} = 3 \)), USB-SPCL6-4 (\( N_{\text{number}} = 6 \) and \( N_{\text{length}} = 4 \)), and USB-SPCL6-5 (\( N_{\text{number}} = 6 \) and \( N_{\text{length}} = 5 \)). The chemical structures of the synthesized USB-SPCLs, including \( N_{\text{number}} \) and \( N_{\text{length}} \), were analyzed using \( ^1 \text{H} \) nuclear magnetic resonance (NMR) spectroscopy. The number-average molecular weights, \( M_n \), the weight-average molecular weights, \( M_w \), and the molecular weight distributions (MWDs) were measured using matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS). More detailed information about the syntheses and general characterizations of USB-SPCLs are provided in our previous publications [14,15].

2.2. Characterization

The glass transitions of USB-SPCLs were measured by differential scanning calorimetry (DSC) using a Netzsch DSC 200 F3 with a heating rate of 20 °C min⁻¹ over the temperature range of −110 to 140 °C under a nitrogen atmosphere. The glass transition temperature, \( T_g \), was determined in each case according to the inflection point in the second DSC curve. The viscoelastic behaviors of USB-SPCLs were observed by dynamic mechanical spectrometry using a stress-controlled rheometer (TA Instruments Inc. AR2000). The AR2000 was operated in a cone-and-plate geometry with a 1° angle and a 60-mm-diameter cone. The gap between the cone and the plate was 80 μm in all measurements. Dynamic frequency sweeps were performed over an angular frequency range of 0.5–100 rad s⁻¹ and the temperature range 30–90 °C, measured in 10 °C intervals. The strain values were determined using a dynamic strain sweep to lie within the linear viscoelastic region.

3. Results and discussion

3.1. Glass transition behaviors of USB-SPCLs

Three- and six-branched USB-SPCLs were prepared with various number of CL repeating units (DP = 2, 3, 4, or 5) in each individual branch initiated from trimethylolpropane (TMP) and dipentaerythritol (DPTOL) cores (Fig. 1). From \( ^1 \text{H} \) NMR and MALDI-TOF-MS measurements (Table 1), it was confirmed that the USB-SPCLs were well synthesized with the desired \( N_{\text{number}}, N_{\text{length}} \), and narrow MWDs (\( M_w/M_n \leq 1.2 \)). Then, the glass transitions of the resulting USB-SPCLs were observed through DSC. As shown in Fig. 2(a), the \( T_g \) values for TMP-cored USB-SPCLs decreased with decreasing \( N_{\text{length}} \), i.e., USB-SPCL3-5 (−64.4 °C) > USB-SPCL3-4 (−64.9 °C) > USB-SPCL3-3 (−65.4 °C) > USB-SPCL3-2 (−65.8 °C), and those for DPTOL-cored USB-SPCLs also had the same tendency (USB-SPCL6-5 (−62.7 °C) > USB-SPCL6-4 (−63.2 °C) > USB-SPCL6-3 (−64.0 °C) > USB-SPCL6-2 (−64.6 °C)). It is generally accepted that a star polymer with a greater number of branches is known to yield a smaller averaged volume (\( V = R^3 \)) and faster molecular mobility at a given total molecular weight [23,24]. In addition, Roovers et al. reported that the \( T_g \) value of a star polymer decreased as the end-group concentration increased due to an increase in the free volume [25,26]. Thus, the end-group concentrations of USB-SPCLs
were evaluated by determining \(N\) number/Mn \[26\]. Among USB-SPCLs with the same \(N\) number, Fig. 2(a) shows that USB-SPCLs with the shorter branched length had higher end-group concentrations than USB-SPCLs with the longer branched length, and, indeed, that USB-SPCLs with the higher end-group concentrations had lower \(T_g\) values than USB-SPCLs with the lower end-group concentrations. These results were consistent with the report by Roovers. However, TMP-cored USB-SPCLs had lower \(T_g\) values than DPTOL-cored USB-SPCLs with the same \(N\) number, even though the end-group concentration of TMP-cored USB-SPCLs is lower than DPTOL-cored USB-SPCLs. In particular, USB-SPCL3-5 and USB-SPCL6-2 exhibited similar \(T_g\) values despite the end-group concentration of USB-SPCL6-2 being about 120% greater than that of USB-SPCL3-5 and despite USB-SPCL6-2 being expected to form a smaller pervading volume due to a high \(N\) number and a low \(N\) length compared with USB-SPCL3-5. These unusual results revealed that the 'traditional' relationship between glass transition behavior and end-group concentration apparently does not apply to our SPCL system with extremely small branches. Instead, Fig. 2(b) shows interestingly that the glass transition behaviors of USB-SPCLs depend on their total molecular weights, not on the molecular architecture features such as \(N\) number and \(N\) length. These results revealed that the extremely small branches in USB-SPCLs cause a new type of molecular dynamic that differs from that of typical star polymers. Actually, Kisliuk et al. reported that star polybutadiene (PB) with unentangled and relatively large arm length (1950 g/mol) exhibited unexpected behaviors, which were \(T_g\), segmental and fast dynamics depending on the total molecular weight but not on its molecular architecture, yet this report did not show the explanation for why such dynamics of PB are manifested \[27\]. Hence, we investigated the dynamics of USB-SPCLs in more detail by observing their viscoelastic behaviors and molecular motions.

3.2. Viscoelastic behaviors and molecular motions of USB-SPCLs

Fig. 3(a) shows the loss tangent, tan \(\delta\) curves for USB-SPCLs in a given angular frequency, \(\omega\), range at the reference temperature \(T_r = 60^\circ\) C. In general, purely viscous behavior (Newtonian viscous liquid) exhibits infinite tan \(\delta\) and purely elastic behavior (Hookean elastic solid) exhibits zero tan \(\delta\) \[28–30\]. As shown in Fig. 3(a), the order of the tan \(\delta\) curves for USB-SPCLs from the upper-right to the
lower-left was USB-SPCL3-2 > USB-SPCL3-3 > USB-SPCL3-4 = USB-SPCL6-2 > USB-SPCL6-3 > USB-SPCL6-4 > USB-SPCL6-5. The tan δ curves for USB-SPCLs in the other temperature range (30–90 °C) showed the same trends (data not shown). Thus, USB-SPCL3-2 was thought to be the most viscous and USB-SPCL6-5 was thought to be the least viscous among them. USB-SPCL3-4 and USB-SPCL6-2 or USB-SPCL6-3 and USB-SPCL6-3 showed intermediate viscous properties with a similar tan δ values. Interestingly, this order of the tan δ curves for USB-SPCLs was reversely consistent with the order for their total molecular weights. This indicated that the viscoelasticity of USB-SPCLs depended on their total molecular weights, regardless of the structural factors of USB-SPCLs such as \(N_{\text{number}}\) and \(N_{\text{length}}\). Such total-molecular-weight-dependent viscoelasticity of USB-SPCLs is a very distinctive observation when considering that the viscoelasticity of typical star polymers with relatively long branches has a dependency on the length of branch [8–13]. Thus, the degree of viscoelasticity for USB-SPCLs was investigated using modified double-logarithmic Cole–Cole plots of the shear loss modulus (viscous behavior), \(G''(\omega)\), versus the shear storage modulus (elastic behavior), \(G'(\omega)\), in a given frequency range at temperatures varying between 30 and 90 °C (Fig. 3(b)). The modified Cole–Cole plots of all USB-SPCLs were located above and to the left of a 45°-sloped straight line drawn at \(G''(\omega) = G'(\omega)\), that is, \(G''(\omega) > G'(\omega)\), indicating that all USB-SPCLs exhibited a viscous response-dominant feature [31–33]. The modified Cole–Cole plots of each USB-SPCL did not vary with temperature in the range measured and the slopes for these plots were 0.5, indicating that structural changes of USB-SPCL, such as melting, crystallization and aggregation, did not occur in this temperature range [34]. These results from Cole–Cole plots were considered that USB-SPCLs had terminal flow behaviors from room temperature [31–34]. In addition, the order of the modified Cole–Cole plots from the upper-left to the lower-right was USB-SPCL3-2 > USB-SPCL3-3 > USB-SPCL3-4 = USB-SPCL6-2 > USB-SPCL6-3 = USB-SPCL6-3 > USB-SPCL6-4 > USB-SPCL6-5, following the reverse order of their total molecular weights. This showed that the degree of viscoelasticity of USB-SPCLs in the terminal flow condition also followed the total molecular weights regardless of the structural factors, consistent with the results from the tan δ curves for USB-SPCLs.

The viscoelastic master curves for USB-SPCLs were obtained from the viscoelastic curves of USB-SPCLs in a given frequency range at various temperatures (see Supplementary Fig. S1) using the time-temperature superposition principle (TTSP) over the entire temperature range measured [34]. As shown in Fig. 4, all of the \(G''(\omega)\) or \(G'(\omega)\) data for USB-SPCLs in the measured temperature range were superposed fairly well at the reference temperature \(T_r = 60^\circ\text{C}\) using only horizontal shift factors, \(\delta_T\), that were obtained based on the zero-shear-rate viscosity at each temperature divided by the zero-shear-rate viscosity at the reference temperature \((\eta_0(T_r)/\eta_0(T_i))\). All of the viscoelastic master curves for USB-SPCLs increased linearly with increasing frequency, and the superposed \(G''(\omega)\) curves were observed to remain below the superposed \(G'(\omega)\) curves without crossover over the entire frequency range. Moreover, the slopes of the superposed \(G''(\omega)\) and \(G'(\omega)\) curves versus the reduced angular frequency, \(\delta_T\), were determined to be 2 and 1, respectively. Therefore, it was considered that USB-SPCLs exhibited unentangled chain dynamics even at room temperature [31–34].

The viscoelastic behaviors of USB-SPCLs were investigated in further detail by separating viscosity and elasticity. The complex viscosities, \(\eta^*\), of all USB-SPCLs at a given temperature were independent of the angular frequency (Supplementary Fig. S2), indicating a Newtonian fluid without chain entanglement [35]. According to the limiting values of the dynamic moduli \((\eta_0 = \lim G''(\omega)/\omega)\), the \(\omega\)-independent \(\eta^*\) values of USB-SPCLs could change into the zero-shear-rate viscosity, \(\eta_0\) [36]. Fetters et al. described that the \(\eta_0\) value of a star polymer depends on the molecular weight of an individual branched segment without considering the total molecular weight and the number of branched segments, following Equation (1) [3,7,37]:

\[
\eta_0 \propto \left( \frac{M_b}{M_e} \right)^b \exp \left( \nu \frac{M_e}{M_b} \right)
\]

where \(M_b\) is the molecular weight of an individual branched segment, \(M_e\) is the entanglement molecular weight, and \(b\) and \(\nu\) are parameters on the order of 1. In Equation (1), the \(\eta_0\) values of star polymers are determined by \(M_b\), irrespective of their total molecular weights and \(N_{\text{number}}\), and they increase “exponentially” with increasing \(M_b\) (see Supplementary Fig. S3). However, as shown in Fig. 5(a), USB-SPCLs yielded different \(\eta_0\) values at a given temperature even if USB-SPCLs had the same \(M_b\) (same \(N_{\text{length}}\); TMP-cored) USB-SPCLs exhibited lower \(\eta_0\) values than DPTOL-cored USB-SPCLs with the same \(N_b\) (i.e., USB-SPCL3-2 < USB-SPCL6-2, USB-SPCL3-3 < USB-SPCL6-3, USB-SPCL3-4 < USB-SPCL6-4, and USB-SPCL3-5 < USB-SPCL6-5).
5 < USB-SPCL6-5). These results reveal that the $\eta_0$ values of USB-SPCLs did not follow Equation (1). Instead, the $\eta_0$ values of USB-SPCLs increased linearly with increasing total $M_w$ at a given temperature (see Fig. 5(b)). Since total-molecular-weight-dependent $\eta_0$ behaviors of polymers are generally represented in the dynamics of typical linear polymers, the resulting $\eta_0$ values of USB-SPCLs were applied to the modified Mark–Houwink equation (Mark–Houwink–Sakurada/Berry–Fox relation) for linear polymer melts, as follows [3,7,36–39]:

$$\eta_0 = K M_w^a$$

where $K$ and $a$ are empirical parameters obtained from the slope and intercept of the power law plot, respectively. In general, the $a$ value is $3.4–3.6$ for $M_w$ greater than $M_c$ and $1–2.5$ for $M_w$ less than $M_c$. In the case of USB-SPCLs, the $a$ values at a given temperature were determined to be $1.2–1.62$ without considering their molecular architecture, suggesting that the $\eta_0$ behaviors of USB-SPCLs can be represented by the dynamics of typical unentangled linear polymers. This indicated the total molecular weights of USB-SPCLs were smaller than $M_c$, in good agreement with the results from the viscoelastic master curves for USB-SPCLs. Therefore, the combined results from the zero-shear-rate viscosity and modified Mark–Houwink equation analyses showed that the viscosity

---

**Fig. 4.** Viscoelastic master curves plotting the dynamic moduli $G'(\omega)$ (filled symbol) and $G''(\omega)$ (open symbol) as a function of $\omega$ at 60 °C, for (a) USB-SPCL3-2, (b) USB-SPCL3-3, (c) USB-SPCL3-4, (d) USB-SPCL3-5, (e) USB-SPCL6-2, (f) USB-SPCL6-3, (g) USB-SPCL6-4, and (h) USB-SPCL6-5.

**Fig. 5.** (a) Logarithmic plots of $\eta_0$ versus $M_w$ for USB-SPCLs at various temperatures. (b) Logarithmic plots of $\eta_0$ versus total $M_w$ for USB-SPCLs at various temperatures. (c) Logarithmic plots of $A_C$ and $J_C$ versus total $M_w$ for USB-SPCLs at the reference temperature $T_r = 60$ °C.
behaviors for USB-SPCLs did not follow the model for a typical star polymer but instead followed the model for an unentangled linear polymer, even though USB-SPCLs are star polymers. These unusual dynamics of USB-SPCLs associated with the unentangled-linear-polymer viscosity behaviors were thought to be attributable to the extremely small branches in USB-SPCLs, and thereby the dynamic behaviors of USB-SPCLs can be explained by the Rouse model for linear polymers.

The elastic properties of USB-SPCLs were investigated by the elasticity coefficient and steady-state compliance using the following equations in the Rouse model [23,40-42]:

$$A_G = \lim_{\omega \to 0} \frac{G(\omega)}{\omega^2}$$

(3)

$$f_e^0 = \lim_{\omega \to 0} \frac{G(\omega)}{G(\omega)^2 + \tilde{G}(\omega)^2} = \frac{A_G}{\eta_0}$$

(4)

where $A_G$ is the elasticity coefficient and $f_e^0$ is the steady-state compliance, corresponding to the permanent elasticity. Fig. 5(c) shows that the logarithmic $A_G$ and $f_e^0$ values of USB-SPCLs at the reference temperature ($T_G = 60 \, ^\circ C$) depended linearly on the total $M_w$, as represented in typical linear polymers, regardless of the molecular architecture parameters such as $N_{number}$ and $N_{weight}$. The plots at other temperatures had similar curves (data not shown). According to the Bueche-modified Rouse model for linear polymers, the slope value of $A_G$ versus total $M_w$ curve exhibits 3-4.3 for an unentangled linear polymer and 7.5 for an entangled linear polymer [41,42]. In the case of USB-SPCLs, the slopes of $A_G$ versus total $M_w$ curves at a given temperature were 3.38-4.18, indicating their unentangled-linear-polymer behaviors of $A_G$. In addition, the $f_e^0$ curves for USB-SPCLs were proportional to total $M_w$ without affecting their branched segments. This indicated that USB-SPCLs exhibited unentangled $f_e^0$ behaviors, whereas the $f_e^0$ curves for entangled linear polymers are independent of $M_w$ [23,43,44]. Thus, we thought that the elasticity of USB-SPCLs also followed the Rouse dynamic behaviors of unentangled linear polymers.

The molecular motions of USB-SPCLs were investigated to demonstrate their unusual total-molecular-weight-dependent Rouse dynamic behaviors through their flow activation energies and longest Rouse relaxation times. Fig. 6(a) shows the plots of $\ln \eta_0$ versus 1000/$T$ for each of USB-SPCLs. In Fig. 6(a), the measured temperature ranges were far above $T_G$ ($> T_G + 100 \, ^\circ C$), and the plots were quite good straight lines. The flow activation energies of USB-SPCLs could therefore be derived from the slopes of these plots using the following Arrhenius equation [45,46]:

$$\eta_0 = A \exp\left(\frac{E_a}{RT}\right)$$

(5)

where $E_a$ is the flow activation energy, $R$ is the gas constant, $T$ is the absolute temperature, and $A$ is a constant. The flow activation energy is the energy required to overcome the potential barrier to flow and provides information about the cooperative diffusional motion of polymer segments [47-49]. The order of the determined $E_a$ values for USB-SPCLs was USB-SPCL6-5 (33.1 kJ mol$^{-1}$) > USB-SPCL6-4 (32.9 kJ mol$^{-1}$) > USB-SPCL6-3 (32.4 kJ mol$^{-1}$) > USB-SPCL3-5 (31.7 kJ mol$^{-1}$) > USB-SPCL6-2 (29.8 kJ mol$^{-1}$) > USB-SPCL3-4 (29.0 kJ mol$^{-1}$) > USB-SPCL3-3 (27.5 kJ mol$^{-1}$) > USB-SPCL3-2 (25.4 kJ mol$^{-1}$), indicating that the cooperative diffusional motions of USB-SPCL segments became more rapid as their total molecular weights decreased. These $E_a$ values of USB-SPCLs were also in fair agreement with the $E_a$ values obtained from the plots of $\ln \eta_0$ versus $T_G/T$ (Supplementary Fig. S4), such plots enable to remove the $T_G$ dependence [50]. In addition to the flow activation energy, the longest Rouse relaxation time, which is associated with the coordinated motion of the whole polymer molecule, of each USB-SPCL was obtained by multiplying the viscosity and elasticity, as follows [23,41,51-53]:

$$\tau_R = \eta_0 f_e^0$$

(6)

where $\tau_R$ is the longest Rouse relaxation time. As shown in Fig. 6(b), the $\tau_R$ values of USB-SPCLs were linearly proportional to the total $M_w$ at a given temperature, and the slopes of $\tau_R$ curves were determined to be between 2.25 and 2.56, corresponding to the $a + 1$ values derived from the relationships mentioned above for unentangled linear polymers: $\eta_0 \propto M_w^a$ and $f_e^0 \propto M_w^{a+1}$. Such total-molecular-weight-dependent relaxation of a whole USB-SPCL molecule suggests that the coordinated motion of a whole USB-SPCL molecule was not affected by the individual branched motion. It was thought that the individual branches in a USB-SPCL molecule were dynamically equivalent and that a whole USB-SPCL molecule moved with a simple uni-motion, because the extremely small branches on the scale of 20-40 atoms were smaller than the Kuhn length of their linear counterparts and existed within one dynamic unit (refer Supplementary Fig. S5 and
If several dynamic boundaries were involved in the individual branch and the branches in a USB-SPCL molecule were not dynamically equivalent, USB-SPCL might show the molecular motion depending on the branching length not the total molecular weight, as is represented in typical star polymers [54]. Thus, we presumed that a whole USB-SPCL molecule acts as a dynamically-equivalent unit, i.e., a single coarse-grain unit. In our presumption, the interesting dynamic phenomena of USB-SPCL can be demonstrated by comparison with a typical star polymer with polymeric large branched segments. In Fig. 7, the typical star polymer has several branches, conceptually divided into multiple coarse-grain units, each of which is composed of several monomeric segments. The monomeric segments in a coarse-grain unit are dynamically equivalent and do not represent a valid dynamic motion, and the coarse-grain unit displays an individual Rouse-segmental motion. Thus, the individual branched motion in the typical star polymer is determined by the assembly of individual Rouse-segmental motions, and hence the whole molecular motion of the typical star polymer depends on the several branches moving individually of each other with one central tie point. On the other hand, an individual branch of USB-SPCL is extremely small with only 20–40 atoms and is composed of several monomeric segments without a valid dynamic unit. Instead, a whole USB-SPCL molecule is regarded as a single coarse-grain unit with dynamically-equivalent branches. Therefore, the whole molecular motion of USB-SPCL represents one Rouse-segmental motion of a single coarse-grain unit, resulting in the total-molecular-weight-dependent Rouse dynamics of USB-SPCL.

4. Conclusions

This study demonstrated the unique molecular dynamic behaviors of USB-SPCLs used as model star polymers with extremely small branches. The glass transition, viscoelasticity, viscosity, elasticity, flow activation energy, and longest Rouse relaxation time of USB-SPCLs exhibited the total-molecular-weight-dependent Rouse dynamic behaviors of USB-SPCLs that followed unentangled linear polymer models, instead of typical star polymer behaviors being affected by the number and length of branched segments. This suggests that an extremely small branch in USB-SPCLs is composed of several monomeric segments without a valid dynamic unit and that a whole USB-SPCL molecule represents one Rouse-segmental motion of a single coarse-grain unit with dynamically-equivalent branches. We believe that the unusual results from this study provide new insights into the molecular dynamic behaviors in an extremely small branched system, and this may pave the way for designing new types of branched polymers with unique dynamic behaviors as well as with attractive advantages of high end-group concentration, such as controlling polymer degradation, lowering softening point, and providing miscibility.

Acknowledgment

This work was supported by Research Institute of Advanced Materials, Department of Materials Science and Engineering in Seoul National University.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2015.09.009.

References
