Concentration fluctuation and cooperative chain mobility of hyperbranched poly(ε-caprolactone)s investigated by photon correlation spectroscopy

Jeongsoo Choa, Seung-Yeop Kwakb,*

Research Institute of Advanced Materials (RIAM), and School of Materials Science and Engineering, Seoul National University, San 56-1, Shinlim-dong, Kwanak-ku, Seoul 151-744, South Korea

Hyperstructured Organic Materials Research Center (HOMRC), and School of Materials Science and Engineering, Seoul National University, San 56-1, Shinlim-dong, Kwanak-ku, Seoul 151-744, South Korea

Received 13 February 2004; received in revised form 22 June 2004; accepted 25 July 2004

Available online 20 August 2004

Abstract

Concentration fluctuation and cooperative chain mobility of the hyperbranched poly(ε-caprolactone) (HPCLs) as well as that of the linear poly(ε-caprolactone) (LPCL) in their concentrated solutions in tetrahydrofuran (Cpolymer = 1.0 g/mL) were systematically characterized using photon correlation spectroscopy (PCS). The results were interpreted in conjunction with the architectural characteristics of the HPCLs that are the different lengths of the linear segments and the different branching structures. The HPCLs were synthesized to incorporate the different lengths of the linear segments consisting of 5, 10, and 20 ε-caprolactone units on their backbone chains, and thereby referred to as HPCL-5, -10, and -20, respectively. The relative degrees of branching (DB) of the HPCLs, which is obtained by branching ratio values, were found to be in the order of HPCL-5 < -10 < -20. From the narrow distribution of relaxation times and q2-dependence of relaxation rates, it was verified that the relaxation processes concerned in this study were due to the concentration fluctuations caused by cooperative chain diffusion. The correlation times, \( \tau_c \)'s, and the corresponding apparent activation energies, \( E_a \)'s, which provide a direct evaluation for the molecular mobility, were determined by non-linear curve fittings of measured correlation functions with Kohlrausch-Williams-Watts (KWW) equation and by the Arrhenius fits of temperature dependences of \( \tau_c \)'s, respectively. As a result, cooperative chain mobility of the HPCLs in the concentrated solution state was found to be higher than that of the LPCL, and was enhanced with the shorter linear segments and with the higher relative DBs of the HPCLs.

Keywords: Hyperbranched polymer; Photon correlation spectroscopy; Concentration fluctuation

1. Introduction

It has been well known that a variety of phenomena of polymeric materials depend on the chemical structure and molecular architecture. In contrast, the question of how the polymer molecular structures are responsible for the observed macroscopic properties still remains to be an unsolved mystery. The molecular motion, which is inevitably affected by the chemical and architectural environment of the given molecules and which exerts great influence on the relevant physical/mechanical properties in the end use, has been increasingly considered as one of the key factors characterizing and explaining the correlation between the given molecular structure and the resulting sample properties [1–6]. In general, it is considered as almost an impossible task to characterize the motion of polymeric materials in terms of the three spatial coordinates of individual atoms because they are so large and complex. However, with the introduction of a number of simplifying assumptions or with the consideration of various well-organized models, characterization of molecular motion in high polymers has become feasible. Commonly, the molecular motions in polymeric materials are
divided into three classes according to the scale of motional events: (1) the very localized vibrational and torsional motions of individual atoms and groups of an isolated side chain, (2) the less localized segmental motions of short segments of the chain backbone consisting of a small number of monomer units, and (3) the large-scale cooperative diffusional motion involving large sections of the chain, or even the whole macromolecule [1,7–9].

As the consideration of molecular motion move from higher-frequency localized motion of individual atoms to lower-frequency retarded motions of larger chain units, such as segmental motion and chain diffusion, the observed phenomena change from a resonance to a relaxation form [1]. It is noteworthy that the various types of molecular motion can be quantitatively characterized by means of the term correlation time, \( \tau_c \), which is defined as the average relaxation time required for the motional events [10]. The correlation times usually fall within a range that typically covers 13 decades of time, \( 10^{-9} < \tau_c < 10^2 \) s, depending on the techniques employed to measure them, which in turn emphasizes the different aspects of the molecular motions present [11].

Up to now, a great variety of the different techniques has been applied to study molecular motion. Spectroscopic techniques include nuclear magnetic resonance (NMR) [5,11–13], neutron diffraction [14,15], dielectric relaxation spectroscopy (DRS) [16], photon correlation spectroscopy (PCS) [17], and X-ray PCS [18]. Also, there are conventional techniques that rely on mechanical perturbation; dynamic mechanical relaxation measurements [6,19], acoustic and ultrasonic method [20,21], and the calorimetric approaches [22]. NMR relaxation reflects the modulation events of magnetic dipoles, which are on a local scale and of a relatively low energy, and the correlation times are several orders of magnitude shorter than those from other techniques [5,12,13]. DRS is limited to detecting the motion only for the electric dipole of the chemical bonds in the backbone [16]. PCS has been extensively utilized to study molecular dynamics in both the concentrated polymer solution and the bulk amorphous polymers due to its wide frequency capability, rapid measurement time, and high sensitivity [17,23–26]. The material relaxation processes characterized by PCS are the local segmental relaxation near and above \( T_g \), associated with the microscale fluctuation of the density and the cooperative chain diffusion associated with the fluctuation of the concentration [25,26]. These two different types of molecular motions are also rationalized by the material state changing along with the temperature in dynamic mechanical measurements: i.e. the local segmental relaxation occurring in the intermediate rubbery-plateau region and the cooperative chain diffusion in the terminal flow region [27].

However, previous motional studies have been limited to the conventional polymeric materials such as linear homopolymers and copolymers, and the molecular motions in the new type of supramolecules possessing the specific molecular architectures still lack instructive understanding. One such example is hyperbranched polymer, which has been continuously considered as an important theme in macromolecular engineering due to the advantageous synthetic simplicity together with the unique mechanical, rheological, and compatibility properties [28–33]. In order to develop these hyperbranched polymers into tailor-made materials with high performance and/or novel functionality, it is a prerequisite to elucidate the correlation between the hyperbranched molecular architecture and the unique properties from the viewpoint of molecular motion. Polymer solutions are normally categorized into four groups, according to their range of concentration because concentration plays an important role in hydrodynamic behavior of macromolecular solutions [34]. The first group of solutions is the hydrodynamically ideal solutions, in which the polymer molecules are so far apart from one another that they have no influence on the liquid flow around the vicinity of each molecules. The second group is the dilute solutions, in which macromolecules mutually, significantly influence the liquid flow around the vicinity of each molecule. Despite that, the qualitative characteristic of the liquid flow is still the same as it was in the ideal solutions. When the concentration of polymer is increased, the macromolecular coils tend to fill up all the available volume at some concentration. This is known as overlap concentration, \( C^* \). The third group of solutions are found in the region of semidilute solutions, where \( C > C^* \), the individual macromolecular coils overlap, form many contacts, and become entangled. The fourth group is the concentrated solutions for which the concentration is relatively higher than the overlap concentration. In these solutions, the individual polymer segments belonging to different chains and/or distant parts of the same chain are packed very closely to one another, and solvent molecules are distributed uniformly among them. In semidilute and concentrated solutions, the simplified rules of hydrodynamic interaction used in ideal and dilute solutions are no longer sufficient and thus, need to be replaced by other concepts. For example, the relative movement of solvent and polymer chain is best treated as permeation or diffusion, and the mutual movement of macromolecules is becoming more dominated by a reptating movement along their contours [35,36]. Notwithstanding the great significance of this issue, only few studies have been done on the solution dynamics of hyperbranched polymers in conjunction with their increased overlap concentration with the increase in the DB, and to our knowledge there have not been any comparative studies conducted on the dynamics of concentrated solutions of hyperbranched polymers and bulk polymer melts.

Here, we synthesized hyperbranched poly(\( \epsilon \)-caprolactone) (HPCLs) with molecular architectural variation, which is the different length of the homologous oligo(\( \epsilon \)-caprolactone) backbone segments consisting of 5, 10, and 20 of \( \epsilon \)-caprolactone monomer units, without significant
variation in the molecular weights. They are, thereby, referred to as HPCL-5, -10, and -20, respectively. The relative degree of branching (DB) of the HPCLs were characterized by the branching ratio values obtained from the ratios of mean-square radius of gyration of each HPCL to that of their linear counterpart, linear poly(ε-caprolactone)s (LPCL). In order to verify the relaxation process of concentrated fluctuation, the distribution of relaxation times and \( q^2 \)-dependence of relaxation rates were characterized by PCS. The cooperative chain mobility of the HPCLs and LPCL in their concentrated solution state was determined by means of the average relaxation time and the apparent activation energy. The objectives of this study are mainly concerned with elucidating the relaxation process of the HPCLs and LPCL solutions in THF, and comparing the cooperative chain mobility in conjunction with the specific molecular architectural difference among the HPCLs and LPCL as well as the relative DB.

2. Experiments

2.1. Materials

The initiator 1, 2,2-bis-(hydroxymethyl)propyl benzoate, for the ring-opening polymerization of ε-caprolactone (ε-CL) was prepared by nucleophilic substitution of potassium salt of 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) with benzyl bromide. Benzyl-protected AB2 macromonomers 2, 2,2-bis[ω-hydroxy oligo(ε-CL)methyl] propyl benzoates, were prepared to incorporate various lengths of oligo(ε-CL) segments by the ring-opening polymerization of ε-CL using a catalytic amount of tin(II) 2-ethylhexanoate (Sn(Oct)\(_2\)) with controlled monomer-to-initiating hydroxyl group molar ratio (ε-CL\(_n\)/[–OH]\(_0\)). Then, hydrogenolysis under hydrogen (H\(_2\)) atmosphere using a palladium on activated carbon (Pd/C. 5 wt% Pd) catalyst was performed to produce \( ω \)-carboxylic-ω-dihydroxy AB2 macromonomers 3, 2,2-bis[ω-hydroxy oligo(ε-CL)methyl] propionic acid. 3 together with p-toluenesulfonic acid (TSA) were added to a three-necked 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 with removing water formed. After 2 h, the argon stream was turned off, and the flask was sealed and connected to a vacuum line (10\(^{-2}\) Torr, cooling trap) for 3 h. After the reaction was completed, the mixture was dissolved in tetrahydrofuran (THF) and precipitated into methanol (MeOH) to give hyperbranched poly(ε-CL)s (HPCLs) 4 as white solids. The structural verification of synthesized materials has been described elsewhere [37–40]. In order to investigate and compare the role of hyperbranched structure against conventional linear structure, linear poly(ε-CL) (LPCL), whose chemical structure and molecular weight is similar to those of the HPCLs, was commercially purchased and used as a linear counterpart to the HPCLs.

2.2. General characterization

The chemical structures of synthesized materials were analyzed by \(^1\)H NMR spectroscopy using a Bruker Avance DPX-300 spectrometer with the tetramethylsilane (TMS) proton signal as an internal standard in CDCl\(_3\). The size exclusion chromatography connected to the multi-angle laser light scattering (SEC-MALLS) was used for the determination of the molecular weights and molecular weights distribution of polymers. An SEC modular system consisted of a Dionex DG-1210 degasser, a Dionex P680 HPLC pump, a Dionex automatic sample injector, and a set of five size exclusion columns (Ultra-micro Styragel\(_6\), 10\(^5\)×2, 10\(^3\), 10\(^3\), 500 Å). A MiniDAWN (Wyatt technology, USA) MALLS detector equipped with 690 nm semiconductor laser was connected between the size exclusion columns and a Wyatt Optilab DSP differential refractometer. The software Astra (ver. 4.90.04, Wyatt technology, USA) was used to compute the calibration curves and the molecular weights distribution. The calibration of detectors was achieved using polystyrene standards of narrow molecular weights distribution and known molecular weights. The differential refractive index increment (dn/dc) in a mixed solvent (THF/DMF 10/1 v/v, and LiNO\(_3\) 2 g/L) at 25°C was determined for poly(ε-CL) with a Wyatt Optilab DSP interferometric differential refractometer, operated at 690 nm and calibrated with aqueous NaCl solutions. The radii of gyration (\( R_2 \)) of three HPCLs and an LPCL were measured by small angle X-ray scattering (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 Kz (\( λ = 1.54 \) Å) radiation, and the scattering angle range was 0.5–2.5°. In the measurement of a THF solution (1 mg/mL) of the sample, the solution was injected into glass capillary in liquid sample holder frame. The background correction was carried out using pure THF solvent.

2.3. Photon correlation spectroscopy (PCS)

PCS measurements were conducted on a Photal DLS 7000 spectrometer, using a 488 nm Argon ion laser operating at 70 mW. All measurements were performed at temperatures ranging from 303 to 333 K at scattering angles of 45°, 90°, and 135°. The time variations in the scattered intensity, \( I(t) \), was analyzed to determine the intensity autocorrelation function, \( g_2(t) \), using a Photal GC 1000 autocorrelator. The normalized form of intensity autocorrelation function, \( g_2(t) \), is given as follows:

\[
g_2(t) = \frac{\langle I(t)I(t + \tau) \rangle}{\langle I(t) \rangle^2}
\]

where \( \tau \) is the delay time and the brackets represent a time average. Here, the measured \( g_2(t) \) is normalized by the
experimental baseline intensity at long delay time. The theoretical normalized field autocorrelation function, \(g_1(t)\), is correlated with \(g_2(t)\) by Siegert relation as follows:

\[
g_2(t) - 1 = f|g_1(t)|^2
\]

where \(f\) is a instrumental factor accounting for deviation from ideal correlation. The solvent-nonsolvent fractionation (THF-cold MeOH) was repeated several times to generate samples with better optical quality. The solutions in THF were filtered several times through 0.45 \(\mu\)m pore diameter Millipore membranes into dust-free cells, and were dried under vacuum. Finally, the sample solutions of desired concentration of 1.0 \(\text{g/mL}\) were prepared by adding accurate amount of pre-filtered dust-free THF in cells.

### 2.4. Steady-shear rheometry

Steady-shear viscosity measurements were performed on a TA instruments AR 2000 constant-stress rheometer using a cone-and-plate geometry with a 2\(^{\circ}\) angle and 6 cm diameter cone. The temperature was controlled by a Peltier lower plate with a precision of 0.1 \(^{\circ}\)C, and the measurements were performed between the temperatures ranging from 60 to 120 \(^{\circ}\)C and at regular intervals of 10 \(^{\circ}\)C. In order to minimize the effect of the thermal expansion of the rheometer, the gap between the cone and the plate was automatically controlled for all temperatures to 56 \(\mu\)m. The range of shear rate measured was from 0.1 to 100 \(\text{s}^{-1}\).

### 3. Results and discussion

#### 3.1. Synthesis and structural characteristics

The syntheses of the AB\(_2\) macromonomers 3 and the hyperbranched poly(\(\varepsilon\)-CL)s (HPCLs) 4 were performed according to a reaction first developed by Trollás et al. [39]. The syntheses were recently modified in our previous work, in which the HPCLs were successfully produced via polycondensation with continuous water removal and the synthetic process was controlled in the manner of less sensitive to the moisture [40] (Scheme 1). The general characteristics of three HPCLs and their linear counterpart, LPCL are listed in Table 1. The average number of \(\varepsilon\)-caprolactone monomer units incorporated in the AB\(_2\) macromonomers, \(\langle N_{\varepsilon-\text{CL}}\rangle\), indicating the average lengths of the linear oligomeric segments, was calculated from the ratios of the integrated area of the peak corresponding to the repeating methylene units (–COCH\(_2\), \(\delta\) 2.22) to the integrated area of the peak corresponding to the chain ends (–CH\(_2\)OH, \(\delta\) 3.59) in \(^1\)H NMR spectra of the AB\(_2\) macromonomers. The calculated \(\langle N_{\varepsilon-\text{CL}}\rangle\) values were found to be in close agreement with the targeted values.

Molecular weights and polydispersity indices of three HPCLs were determined by size exclusion chromatography (SEC) with multi-angle laser light scattering (MALLS) detector, as listed in Table 1. Hyperbranched polymers are generally considered to give inaccurately low molecular weight characterization by conventional SEC analysis based upon linear standards due to decreased hydrodynamic volume imposed by branching [42]. The molecular weight values for the HPCLs determined by SEC-MALLS were determined to be near the absolute values in our previous study [40], in which molecular weights determined by \(^1\)H NMR end-group analysis, conventional SEC, and SEC-MALLS were compared. As shown in Table 1, the number average molecular weights of three HPCLs were not significantly varied and were, in fact, found to be similar to that of the LPCL.

The DB, which is one of the most important characteristic for describing the architectural features of the hyperbranched polymers, 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 a given hyperbranched polymer. As indicated in Fig. 1(a), intrinsically attached long oligo(\(\varepsilon\)-CL) segments in the branching point creates D, L, and T units of which chemical environments are not significantly different each other, and thus, gave neither distinguishable \(^1\)H resonance peaks useful for the calculation of DB nor quaternary carbons...
unique for determining the DB. Therefore, the information about DB of the HPCLs were alternatively achieved from the values of branching ratio, \( g \) [43], that were calculated from the ratio of mean-square radius of gyration between a given HPCL and the reference LPCL:

\[
g = \frac{\langle R_g^2 \rangle_{\text{branched}}}{\langle R_g^2 \rangle_{\text{linear}}} 
\]

(3)

It is worthy to note that the parameter \( g \) is always less than one and decreases with the increase in DB as the branched molecules become more compact compared to the less branched molecules or the corresponding linear counterpart of the similar molecular weight in the completely dissolved solution state [44]. The radii of gyration (\( R_g \)'s) of the HPCLs and LPCL were determined by small angle X-ray scattering (SAXS) using typical Zimm plots (represented as \( I/I(q) \) versus \( q^2 \) where \( I(q) \) and \( q \) are the experimental scattered intensity and the scattering vector, respectively), in which the scattered curves for the HPCLs and LPCL appear linear over a relatively large \( q \) range. This result is in good agreement with the previous results of Prosa et al., in which it was reported that the SAXS curves of hyperbranched polymers were fitted much better by the Zimm particle scattering function, while those of dendrimers were better fit by the Guinier function [45].

The determined \( R_g \) values for the HPCLs and LPCL are listed in Table 2 together with the calculated branching ratios. Recognizing that the relative DB increases with the decrease in branching ratio, it was concluded that the relative DB increased in the order of HPCL-20 > HPCL-10 > HPCL-5, indicating that the relative DB increases as

![Scheme 1.](image-url)

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>AB2 macromonomers</th>
<th>Entry</th>
<th>([\varepsilon-\text{CL}]/[\text{–OH}]_0^a)</th>
<th>(\langle N_{\text{cl}} \rangle^b)</th>
<th>(\langle N_{\text{AB2}} \rangle^c)</th>
<th>(M_w^d)</th>
<th>(M_w/M_n^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPCL-5</td>
<td>AB2-5</td>
<td>5</td>
<td>5.7</td>
<td>8.1</td>
<td>11,800</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>HPCL-10</td>
<td>AB2-10</td>
<td>10</td>
<td>10.3</td>
<td>5.1</td>
<td>12,600</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>HPCL-20</td>
<td>AB2-20</td>
<td>20</td>
<td>20.1</td>
<td>3.3</td>
<td>15,700</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>LPCLe</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10,700</td>
<td>1.4</td>
<td></td>
</tr>
</tbody>
</table>

a \( \varepsilon \)-Caprolactone monomer-to-initiating hydroxyl group molar ratio.

b Average number of \( \varepsilon \)-caprolactone units incorporated in the AB2 macromonomers.

c Average number of the AB2 macromonomer units incorporated in the HPCLs.

d Obtained from SEC-MALLS.

e Linear poly(\( \varepsilon \)-caprolactone) (Aldrich Chemicals).
the length of linear oligo(ε-CL) segments incorporated in the backbone chains become shortened. More details on the determination of branching ratios of the HPCLs have been described in our previous study [40].

To rationalize the macromolecular dynamics of sample solutions which will be discussed in the later section, the overlap concentration, $C^*$, for each HPCL and LPCL was calculated through the following equation [46]:

$$C^* = \frac{M}{(4/3)\pi N_A R_g^3}$$  \hspace{1cm} (4)

where $M$ is the molecular weight of the polymer, $N_A$ is the Avogadro’s number, and $R_g$ is the radius of gyration of the polymer chain. The resulting $C^*$ values and reduced concentrations, $C/C^*$, of sample solutions are listed in Table 2. Although the molecular weights of HPCLs and LPCL are not significantly different and the concentrations of sample solutions remain the same ($C = 1$ g/mL), the reduced concentration for each sample solution was found to vary significantly due to decreased radii of gyration with the increase in the relative DB of HPCLs as described in the previous section.

### 3.2. Concentration fluctuation and cooperative chain mobility

Fig. 2 illustrates the typical intensity autocorrelation functions, plotted as $g_2(t)$-1 versus $t$, for the concentrated solution of the HPCLs and LPCL in THF (polymer/THF, $C_{\text{polymer}} = 1.0$ g/mL) measured at 303 K and a scattering angle of 90°. Solid lines in Fig. 2 are the fits to the single Kohlrausch-Williams-Watts (KWW) equation as shown below [47,48]:

$$g_1(t) = \exp \left[ -\left(\frac{t}{\tau_{\text{KWW}}}ight)^\beta \right]$$  \hspace{1cm} (5)

treating $\tau_{\text{KWW}}$ and $\beta$ as adjustable parameters. Here, $\tau_{\text{KWW}}$ indicates the relaxation time and $\beta (0 < \beta \leq 1)$ is a measure of the width of the distribution of the relaxation time. The parameter $\beta$ equals unity for a single exponential and decreases as the width of the distribution becomes broader. As clearly seen in Fig. 2, autocorrelation functions for the HPCL/THF solutions and the LPCL/THF solution appear to fit very well by means of the single KWW equation. The resulting parameters, $\tau_{\text{KWW}}$ and $\beta$ are listed in Table 3. The distribution of relaxation times can be also determined by performing well-known inverse Laplace transform (ILT) as shown below [49]:

$$g_1(t) = \int_{-\infty}^{\infty} \exp(-t/\tau)L(\ln \tau)d\ln \tau$$  \hspace{1cm} (6)

where $L(\ln \tau)$ is the distribution of the relaxation times. The corresponding relaxation time spectra, $L(\log \tau)$ plotted against $\log \tau$, were obtained from the ILT analyses on $g_1(t)$’s for the HPCL/THF solutions and the LPCL/THF solution as shown in Fig. 3. A single feature is clearly present in these spectra, which indicates that there exists only one relaxation process for all concentrated solution samples. In addition, the distribution of relaxation times appear to relatively narrow, which is in good agreement with the determined $\beta$-values. The narrow distributions of relaxation times determined from the $L(\ln \tau)$ spectra as well as from the $\beta$ values being near 1 indicate the typical relaxation of concentration fluctuation far above $T_g$ via

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_g$ (nm) $^a$</th>
<th>$G$</th>
<th>$C^*$ (mg/mL)</th>
<th>$C/C^*$ $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPCL-5</td>
<td>4.57</td>
<td>0.76</td>
<td>87</td>
<td>11.5</td>
</tr>
<tr>
<td>HPCL-10</td>
<td>4.77</td>
<td>0.83</td>
<td>75</td>
<td>13.4</td>
</tr>
<tr>
<td>HPCL-20</td>
<td>5.18</td>
<td>0.98</td>
<td>69</td>
<td>14.5</td>
</tr>
<tr>
<td>LPCL</td>
<td>5.23</td>
<td>1</td>
<td>42</td>
<td>23.7</td>
</tr>
</tbody>
</table>

$^a$ Determined from SAXS curves fit by Zimm scattering function.

$^b$ $C = 1$ g/mL.
cooperative chain diffusion [50], which is also probed by the measurements of $q^2$-dependence of relaxation rates.

In order to rule out the possible contribution to the relaxation processes, angular-dependent experiments for the HPCL/THF solutions and the LPCL/THF solution were carried out at three scattering angles ($45^\circ$, $90^\circ$, and $135^\circ$) over the temperature range $303 < T < 333$ K. While in the dilute polymer solution ($C_{\text{polymer}} = 0$), the concentration fluctuations were accounted for by a translational diffusion mechanism, and the relaxation rates are $q^2$-dependent [24, 26, 51]. In the bulk or as the concentration increased beyond the semidilute region, the diffusion of the center-of-mass of the polymer chain drastically slowed down. Here, the localized segmental motion leading to the structural relaxation plays a dominant role in the scattering spectrum. Scattering from localized segmental motion in the concentrated polymer solution or in the bulk were found to be $q^2$-independent [24, 26, 51]. However, it was also reported that even in the concentrated solution or in the bulk state, the fast process due to density fluctuation (segmental relaxation) shifted out of the correlator window at high temperature range ($T \gg T_g$), and the concentration fluctuation became dominant [24, 26]. Fig. 4 shows the $q^2$-dependences of the relaxation rates for the concentrated solutions of the HPCLs and LPCL. Although the solution samples of the HPCLs and LPCL were highly concentrated ($C_{\text{polymer}} = 1$ g/mL), the relaxation rates were all $q^2$-dependent, which indicates that the relaxation processes of the concentration fluctuation are governed by cooperative chain diffusive motion, providing that the range of experimental temperatures were far above the glass transition ($T \gg T_g$) [26, 46]. Therefore, it was enabled to estimate the cooperative diffusion coefficient in the laboratory frame, $D_c$, from the slopes of straight line

Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>$D_c \times 10^{11}$ (cm$^2$/s)</th>
<th>$\tau_c$ (s)</th>
<th>$E_a$ (kJ/mol)</th>
<th>$E_h$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPCL-5</td>
<td>13.2</td>
<td>0.26</td>
<td>13.7</td>
<td>34.4</td>
</tr>
<tr>
<td>HPCL-10</td>
<td>9.0</td>
<td>0.38</td>
<td>14.0</td>
<td>35.4</td>
</tr>
<tr>
<td>HPCL-20</td>
<td>7.2</td>
<td>0.47</td>
<td>15.7</td>
<td>37.1</td>
</tr>
<tr>
<td>LPCL</td>
<td>6.1</td>
<td>0.56</td>
<td>17.1</td>
<td>39.8</td>
</tr>
</tbody>
</table>

* Measured at 303 K.
shown in Fig. 6 by means of following relation [50]:

\[ \Gamma = D_c q^2 \]  

(7)

where \( \Gamma \) is the relaxation rate (\( \Gamma = \tau^{-1} \)). The determined values of \( D_c \) for concentrated solution samples measured at 303 K are listed in Table 3. Here, it was found that \( D_c \) was affected by the difference in the molecular architecture of the HPCLs and LPCL as \( D_c \) decreased with the increase in the length of linear segments and with the decrease in the relative DB. The decrease in \( D_c \) is due to reduced chain diffusive mobility of polymer samples.

In order to characterize and compare the cooperative chain mobility in the concentrated solution state more quantitatively, the correlation time, \( \tau_c \), which is defined as the average time required for motional events, and the apparent activation energy, \( E_a \), which corresponds to the barrier height for the potential hindering motion, was estimated from the average relaxation time and the temperature dependence of \( \tau_c \)'s, respectively. Fig. 5 illustrates \( g_2(t) \)-1 versus \( t \) plots for the concentrated solution of the HPCL-10 (\( C_{\text{HPCL-10}} = 1.0 \text{ g/mL} \)) measured at temperatures ranging from 303 to 333 K. As shown in Fig. 5, \( g_2(t) \)'s for the HPCL-10/THF solution measured in this temperature range exhibited typical exponential decay curves, which can be represented well by single KWW approximation (Eqs. (2) and (5)). The \( \tau_c \)'s for all concentrated solution samples were determined from the parameters, \( \tau_{\text{KWW}} \) and \( \beta \) resulted by KWW fits as follows [49]:

\[ \tau_c = \tau_{\text{KWW}} \cdot \frac{1}{\beta} \int_0^{+\infty} \exp \left[ -\left( \frac{t}{\tau_{\text{KWW}}} \right) \beta \right] \, dt \]

\[ = \frac{\tau_{\text{KWW}}}{\beta} \Gamma \left( \frac{1}{\beta} \right) \]  

(8)

where \( \Gamma \) is the gamma function. Fig. 6 exhibits the determined \( \tau_c \)'s for the HPCL/THF solutions and the LPCL/THF solution as a function of temperature. Throughout the entire range of experimental temperatures, the \( \tau_c \)'s were in increasing order of HPCL-5/THF<HPCL-10/THF<HPCL-20/THF<LPCL/THF, which indicates that the cooperative chain diffusive mobility of the HPCLs was higher than that of the LPCL in their concentrated solution state, and among the HPCLs it was observed to enhance with the increase in the relative DB. Further insights into Fig. 6 by fitting the \( \tau_c \)'s to the Arrhenius equation provided novel information about the temperature dependence of the molecular motion and the \( E_a \) of the hyperbranched polymers with the different nature of branching structure, i.e. the different DB and the different length of linear oligo(\( \varepsilon \)-caprolactone) segments. The solid lines in Fig. 6 represents the fits of the \( \tau_c \)'s to the Arrhenius equation as follows:

\[ \log \tau_c = \log \tau_{c,0} + \frac{E_a}{2.303RT} \]  

\[ \frac{1}{1000/T} (K^{-1}) \]

where \( R \) is the gas constant and \( \tau_{c,0} \) is the preexponential factor. The determined values of \( E_a \) as well as \( \tau_c \) are summarized in Table 3, and are represented in Fig. 7 as a function of relative DB as well as \( \langle N_{-\text{CL}} \rangle \) to visualize the difference in cooperative chain mobility of the HPCLs and LPCL in their concentrated solution state. As shown in Fig. 7, the \( E_a \)'s of the HPCL/THF solutions were lower than that of the LPCL/THF solution, and moreover, were observed to
reduce with the increase in the relative DB of the HPCLs, which in turn is in good agreement with the $\tau_c$ results.

The dynamics of polymer solutions in semidilute ($C > C^*$) and concentrated solution region ($C \gg C^*$) are often described using the reptation concept of de Gennes [35,36]. Using the tube model, the relaxation time of a single reptating chain in an entangled solution of linear polymers was found to scale according to $T_r \sim N^3 C^{3/2}$ where $N$ is the polymerization index of polymer [52]. On the other hand, the reptating motion of branched polymers is known to be strongly restricted by the chains as it requires a considerable decrease in entropy to cause a substantial portion of a branch to lie parallel to the main chain in an adjacent tube [53,54]. However, all the results of cooperative diffusion constants, average relaxation times at a given temperature and activation energies of present study showed that the cooperative chain motion occurs at a faster rate in the solution of HPCLs with higher DB as indicated in Table 3. This can be explained by the decrease in the $C/C^*$ of solutions of HPCLs with a higher DB because the individual polymer segments belonging to different chains and/or distant parts of the same chain must be packed less closely, giving more space for chain movement in solution with lower $C/C^*$ [34].

### 3.3. Cooperative chain mobility of bulk polymer melt

Motion characteristics of concentrated solutions of HPCLs and LPCL were compared with the cooperative chain motion of bulk polymer melt. Steady-shear melt viscosities of HPCLs and LPCL were measured in the shear rate range from 0.1 to 100 s$^{-1}$ at different temperatures ranging from 60 to 120 °C and at a fixed interval of 10 °C. Fig. 8 shows the exemplary results of steady-shear viscosity for HPCLs and LPCL measured at 90 °C. For all HPCLs and LPCL, the viscosity was found to be independent of shear rate, which is characteristic of a Newtonian fluid.

The temperature dependences of the viscosity of HPCLs and LPCL are illustrated in Fig. 9. From this figure, it was verified that HPCLs and LPCL exhibit good linear relationships between $\ln \eta$ and $1/T$ within the temperature range employed, which is in good agreement with the kinetic rate theory of flow as represented by the Arrhenius-Frenkel-Eyring type equation as follows [55]:

$$\ln \eta = A + \frac{E_h}{RT}$$

(10)

The observed linearity of $\ln \eta$ versus $1/T$ relationships indicates that the apparent activation energy of flow, $E_h$, can be determined by the slopes of these plots. The derived $E_h$ values for HPCLs and LPCL are summarized in Table 3. According to the kinetic theory of flow, the lower activation energy of flow corresponds to the faster cooperative diffusive motion of bulk polymer chain in the melt [1,9]. As shown in Table 3, the cooperative diffusive motion of polymer chains in their melt state is faster in the order of...
relaxation rates for all concentrated solution samples were in good agreement with the cooperative diffusive motion of polymer chains in their concentrated solution state as described in the previous section.

4. Conclusion

In the present study, three hyperbranched poly(ε-CL)s (HPCL-5, HPCL-10, HPCL-20) with molecular architectural variations in terms of lengths of the homologous oligo(ε-CL) segments and hence the different relative DBs, were prepared without significant variation in the molecular weights. The cooperative chain mobility of these HPCLs and their linear counterpart, LPCL, was characterized in their concentrated solution state (C = 1.0 g/mL in THF) by the PCS technique, and compared with the cooperative chain mobility of bulk polymer in their melt state. The ratio of mean-square radius of gyration of each HPCL to that of the LPCL, which is known as the branching ratio, resulted in the relative DB for individual HPCL. The relative DBs of the HPCLs were found to be considerably influenced by the length of linear oligo(ε-CL) segments; the shorter the oligo(ε-CL) segments, the higher relative DB in the order of HPCL-5 > HPCL-10 > HPCL-20. The overlap concentrations of HPCLs were higher than that of LPCL, and was observed to become higher with the increase in the relative DB, which in turn resulted in the reduced concentrations of sample solutions of the present study in the following order: HPCL-5/THF < HPCL-10/THF < HPCL-20/THF < LPCL/THF.

The measured autocorrelation functions for the concentrated solution of the HPCLs and LPCL in THF were analyzed using KWW equation as well as inverse Laplace transform. The results exhibited narrow distribution of relaxation times, which is the characteristic relaxation of concentration fluctuation via cooperative chain diffusion. The angle-dependent PCS measurements revealed that the relaxation rates for all concentrated solution samples were q²-dependent over the range of experimental temperatures, which is also characteristic of concentration fluctuation. The correlation time, τc, was determined by applying the nonlinear curve fittings of g1(t)'s to the KWW equation, which also provided a unique means to evaluate molecular mobility. From the τc measurements, we concluded that the cooperative chain mobility of the HPCLs was higher than that of the LPCL in their concentrated solution state, which then enhanced with shorter linear segments and with higher relative DBs of the HPCLs throughout the entire experimental temperature range. The apparent activation energy, E_a, was determined from the temperature dependence of the τc's and the Arrhenius equation. The order of E_a's was in good agreement with the trend in τc's, indicating a higher cooperative chain mobility as the hyperbranched structures were endowed and as the relative DBs increased. A faster cooperative chain mobility of HPCLs than LPCL and faster mobility of HPCLs with higher DB in their solution state can be explained by the lower reduced concentration of solutions of HPCLs with higher DB because polymer chains must be packed further apart from one another so as to allow chains to move more freely. Cooperative chain mobility of bulk HPCLs and LPCL in the melt state was found to be in good agreement with mobility in the concentrated solution state.

Acknowledgements

The authors are grateful to the Ministry of Environment, Republic of Korea for their support through Eco-Technopia 21 project.

References
