Non-Isothermal Crystallization of Hyperbranched Poly(ε-caprolactone)s and Their Linear Counterpart

Jeongsoo Choi, Sang-Wook Chun, Seung-Yeop Kwak*

Hyperstructured Organic Materials Research Center (HOMRC), and School of Materials Science and Engineering, Seoul National University, San 56-1, Shillim-dong, Gwanak-gu, Seoul 151-744, Korea
Fax: (+82) 2 885 1748; E-mail: sykwak@snu.ac.kr

Received: March 18, 2006; Accepted: May 2, 2006; DOI: 10.1002/macp.200600129

Keywords: crystallization; hyperbranched; poly(ε-caprolactone); structure–property relations

Introduction

Non-isothermal crystallization has drawn considerable attention in the field of polymer science and engineering since it approaches more closely to the industrial conditions of polymer processing such as extrusion, molding, and melt spinning of synthetic fibers.[1–3] Although numerous studies have been carried out on polymer crystallization so far, the focus has only been on the different effects observed during the isothermal crystallization, since theoretical analysis of isothermal crystallization data is relatively simple. There have only been a few publications that were directly related with the quantitative evaluation of kinetic parameters for non-isothermal crystallization because the treatment of dynamic crystallization data is rather complicated.[4,5] Moreover, to our knowledge, there have been very few studies conducted on the non-isothermal crystallization behavior of molecules possessing complex architectures such as hyperbranched polymers (HBPs) as well as their architectural effect on the crystallization kinetics even though they are very important topics for designing novel materials with unique properties and to optimize their processes.

HBPs are irregular analogs of dendrimers that have a well-defined and perfectly branched structure. Although dendrimers are prepared through divergent or convergent approaches composed of a step-by-step synthesis, HBPs are prepared by a direct one-pot polymerization of AB₅-type monomers.[6] Moreover, the three-dimensional globular architecture of HBPs is known to impart various different properties from those of conventional linear polymers such

Summary: Three hyperbranched poly(ε-caprolactone)s were prepared with the architectural variation in the length of linear backbone segments consisting of 5, 10, and 20 ε-caprolactone units (accordingly given the names HPCL–5, –10, and –20, respectively) and in the number of branching points as characterized by 1H NMR end group analyses. The non-isothermal crystallizations of HPCLs and LPCL were performed using DSC at various cooling rates and the kinetic study was further performed by using both Ozawa and Kissinger methods. All the kinetic parameters such as the cooling functions and the apparent activation energy of crystallization indicated that HPCLs with longer linear segments and fewer number of branching points showed faster crystallization rates, whereas LPCL exhibited an intermediate rate between HPCL–10 and HPCL–20, i.e., HPCL–5 < HPCL–10 < LPCL < HPCL–20. The decrease in the crystallization rate is attributed to the presence of heterogeneous branching points in HPCLs with shorter segments, which hinders the regular chain packing to crystallize. In addition, the faster crystallization of HPCL–20 compared to LPCL was associated with the higher cooperative chain mobility in the melt.

Schematic illustrations for HPCL and LPCL.
as less entanglement in the solid state,\textsuperscript{[7]} high solubility in various solvents, low melt viscosity,\textsuperscript{[8–10]} and fast molecular motion.\textsuperscript{[11,12]} This synthetic simplicity, along with the unique physical and chemical properties of HBPs, has resulted in many different architectures being developed for tailor-made materials with high performance and/or novel functionality. Recently, several approaches to the development of HBPs with large versatilities through the introduction of controlled branching units have been reported.\textsuperscript{[13–18]} The synthesis of hyperbranched poly(\(\varepsilon\)-caprolactone (CL)) (HPCL) reported by Hedrick et al. is one such example. In this case, a homologous series of HPCLs were prepared with a range of molecular architectural variations, i.e., different lengths of linear backbone segments and different numbers of branching points.\textsuperscript{[19–21]} Although there have been some advances in the studies on synthetic methods and various characterizations,\textsuperscript{[22–27]} there is still a lack of understanding of the non-isothermal crystallization behavior of HPCLs.

Previously, we have reported synthesis and architectural characterization of HPCLs with different lengths of backbone segments and a different degree of branching.\textsuperscript{[25]} In this study, non-isothermal crystallization experiments were conducted for these HPCLs and their linear counterpart, linear poly(\(\varepsilon\)-caprolactone) (LPCL) using DSC, and further analyzed by both Ozawa and Kissinger approaches. The main objective of this study is to evaluate and compare the non-isothermal crystallization kinetics of HPCLs and LPCL in conjunction with their architectural characteristics and their chain mobility.

Experimental Part

HPCLs were synthesized according to a reaction first developed by Hedrick et al.,\textsuperscript{[20]} and recently modified in our previous study, in which HPCLs were successfully prepared by polycondensation of continuously removing water in a less moisture-sensitive reaction condition.\textsuperscript{[25]} AB\textsubscript{2} macromonomers were prepared to incorporate three different lengths of homologous oligo(\(\varepsilon\)-CL) segments by controlled ring-opening polymerization with variable \(\varepsilon\)-CL to initiating hydroxyl group molar ratio ([L-CL]_{0}/[–OH]_{0} = 5, 10, and 20) followed by hydrogenolysis deprotection, which explains the name given as AB\textsubscript{2}–5, –10, and –20, respectively. HPCLs were prepared by polycondensation of different AB\textsubscript{2} macromonomers, referred to respectively as HPCL–5, –10, and –20 so that they have backbone segments with intrinsically different lengths. Polycondensation reaction was conducted in a three-necked flask equipped with an argon inlet, a drying tube, and a stirrer in the presence of \(p\)-toluene-sulfonic acid (TSA). The reaction mixture was allowed to react at 110 °C under a stream of argon, removing the water formed during the reaction. After 2 h, the argon stream was stopped from purging, and the flask was sealed and connected to a vacuum line (10\textsuperscript{–2} Torr, cooling trap) for 3 h. After the polycondensation reaction was completed, the mixture was dissolved in THF and precipitated into MeOH. The yields of polycondensation reaction were between 87 and 94%, which suggests that unreacted macromonomer might remain in the hyperbranched polymer. Since unreacted macromonomers may act as a plasticizer during crystallization of HPCLs, the removal of unreacted macromonomers in the product mixture is important. In order to remove these unreacted contaminants, the dissolution/precipitation procedure was repeated several times, and it was found to be effective since only minimal traces of macromonomer was observed in the size exclusion chromatography (SEC) chromatogram of HPCL as shown in Figure 1. To compare the role of hyperbranched structure against conventional linear structure, LPCL, whose chemical structure and molecular weight are similar to those of HPCLs, was purchased and used as a linear counterpart of HPCLs. Table 1 provides a list of the general characteristics of these HPCLs and LPCL.

A Mettler DSC-30 differential scanning calorimeter was used to investigate the overall kinetics of non-isothermal crystallization of HPCLs and the LPCL. All sample weights were fixed as 10 mg with an error below 1 mg. The samples were heated to 100 °C under nitrogen gas to suppress the thermal oxidation and were kept for 3 min to eliminate thermal history. Non-isothermal experiments were performed by cooling the aforementioned melt samples at different cooling rates, ranging from 2 to 10 °C·min\textsuperscript{–1}. The weight fraction of crystallized materials at time \(t\), \(X_{c}\), was calculated from the ratio of the crystallization enthalpy generated at time \(t\) to the crystallization enthalpy of a completely crystallized sample. In addition, crystallization peak temperature, \(T_{p}\), was estimated from the peak maximum of the DSC thermogram.

Results and Discussion

The molecular architectural variations among the HPCLs and LPCL in the present study, which are well reflected in Figure 2, are as follows; The lengths of linear oligo(\(\varepsilon\)-CL) segments become longer and the number of branching points in HPCL molecules become fewer in the order of HPCL–5, –10, and –20, while the LPCL is made of one long linear chain of poly(\(\varepsilon\)-CL). Quantitative comparison of the lengths of linear oligo(\(\varepsilon\)-CL) segments and the number of branching points are made by the value of the average

![Figure 1. Size exclusion chromatograms of AB\textsubscript{2} macromonomer (AB\textsubscript{2}–10) and HPCL–10.](image-url)
number of \( \varepsilon \)-CL monomer units incorporated in \( \text{AB}_2 \) macromonomers, \( \langle N_{\varepsilon-\text{CL}} \rangle \), and the average number of \( \text{AB}_2 \) macromonomer units incorporated in HPCLs, \( \langle N_{\text{AB2}} \rangle \). The calculation method of these values is reported in detail in our previous paper.\(^{[25]}\) HBPs are generally considered to give inaccurately low molecular weight characterization by conventional SEC based upon linear standards due to decreased hydrodynamic volume imposed by branching.\(^{[28]}\)

Therefore, the absolute number- and weight-average molecular weights of three HPCLs and LPCL were determined by SEC equipped with multi-angle laser light scattering (MALLS) detector. 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. As indicated in Table 1, the molecular weight distributions of HPCLs were found to be relatively narrow compared to common condensation polymers, which suggests that the transesterification reaction occurred minimally during polycondensation.

For HPCLs and LPCL, the non-isothermal crystallizations were performed by using DSC from their melt state at various cooling rates ranging from 2 to 10 \( ^{\circ} \text{C} \cdot \text{min}^{-1} \) and at an interval of 2 \( ^{\circ} \text{C} \cdot \text{min}^{-1} \). Figure 3 shows the DSC exothermic curves for HPCLs and LPCL at various cooling rates. It shows curves that are typically observed in general crystallizable polymers. The DSC exothermic curves for all HPCLs and LPCL are shifted to the low temperature region as the cooling rate increases. In particular, the crystallization enthalpy peak for each HPCL at a specific cooling rate is observed to shift to the high temperature region as the length of the incorporated linear backbone segments increases and the number of branching points decreases in the following order: HPCL–5 < HPCL–10 < HPCL–20. This shows that the acceleration of crystallization temperature is attributed to the incorporation of the longer linear crystallizable oligo(\( \varepsilon \)-CL) segments onto the HPCL backbone. However, the crystallization exotherms of the LPCL are shown in the region between HPCL–10 and HPCL–20, the origin of which will be described in detail in a later section. The degree of crystallinity, \( X_c \), can be estimated from the enthalpy evolved during crystallization using the following:

\[
X_c(\%) = \frac{\Delta H_c}{\Delta H_m} \times 100
\]  

where \( \Delta H_c \) is the apparent enthalpy of crystallization and \( \Delta H_m \) is the extrapolated enthalpy corresponding to the melting of a 100% crystalline poly(\( \varepsilon \)-CL) sample with an average value of 136.4 J \( \cdot \text{g}^{-1} \).\(^{[29]}\) The peak temperature, \( T_p \), the heat of crystallization \( \Delta H_c \), and \( X_c \) were estimated for all HPCLs and LPCL as a function of a cooling rate and summarized in Table 2. As can be seen in Table 2, \( X_c \) decreases with increase in cooling rate, indicating that the cooling rate is one of the major factors affecting the crystallinity. In addition, it is also observed that the \( X_c \) of HPCLs increases as the lengths of linear backbone segments increase and the number of branching points decrease while the \( X_c \) of LPCL shows intermediate values between HPCL–10 and HPCL–20. Therefore, the introduction of branching architecture with many short branches can be understood to

Table 1. Synthetic conditions and characterization results for HPCLs and LPCL.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Macromonomer entry</th>
<th>( \langle N_{\varepsilon-\text{CL}} \rangle ) (^{[b]})</th>
<th>( \langle N_{\text{AB2}} \rangle ) (^{[c]})</th>
<th>SEC-MALLS (^{[d]})</th>
<th>( E_c ) (^{[e]})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( M_w ) MALLS</td>
<td>( M_m ) MALLS</td>
</tr>
<tr>
<td>HPCL–5</td>
<td>AB( _2 )-5</td>
<td>5.7</td>
<td>8.1</td>
<td>11 800</td>
<td>20 900</td>
</tr>
<tr>
<td>HPCL–10</td>
<td>AB( _2 )-10</td>
<td>10.3</td>
<td>5.1</td>
<td>12 600</td>
<td>20 400</td>
</tr>
<tr>
<td>HPCL–20</td>
<td>AB( _2 )-20</td>
<td>20.1</td>
<td>3.3</td>
<td>15 700</td>
<td>24 200</td>
</tr>
<tr>
<td>LPCL(^{[f]})</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10 700</td>
<td>15 200</td>
</tr>
</tbody>
</table>

\(^{[a]}\) AB\( _2 \) macromonomers used for the preparation of HPCLs.

\(^{[b]}\) Average number of \( \varepsilon \)-CL units incorporated in the AB\( _2 \) macromonomers.

\(^{[c]}\) Average number of AB\( _2 \) macromonomers incorporated in HPCL, \( \langle N_{\text{AB2}} \rangle = m/[2 \times \langle N_{\varepsilon-\text{CL}} \rangle - m] \).

\(^{[d]}\) SEC equipped with MALLS.

\(^{[e]}\) Activation energy of crystallization.

\(^{[f]}\) Commercial grade purchased from Aldrich.
cause deceleration of the crystallization while only a few long branches may accelerate the process. In order to illustrate the effect of the architectural difference on the crystallization, the non-isothermal crystallization kinetics is further investigated using a modeled study as detailed below.

In non-isothermal crystallization at a specific cooling rate, the relative degree of crystallinity, $X_T$, as a function of crystallization temperature, $T$, can be calculated using the following equation:

$$X_T = \frac{\int_{T_0}^{T} (dH_c/dT)dT}{\int_{T_0}^{T_\infty} (dH_c/dT)dT}$$

where $T_0$ and $T_\infty$ are the temperatures at which crystallization commenced and completed, taken at the starting and ending inflections of the crystallization peak, respectively, and $H_c$ is the enthalpy of the process. Based on this equation, $X_T$ at a specific temperature can be calculated, and $X_T$ versus $T$ plots for all HPCLs and LPCL are illustrated in Figure 4. During a non-isothermal crystallization, the crystallization time, $t$, is correlated with the crystallization temperature as follows:

$$t = \frac{T_0 - T}{\gamma}$$

where $T$ is the temperature at crystallization time $t$, and $\gamma$ is the cooling rate employed for non-isothermal crystallization. Combining Equation (2) and (3), Figure 4 can be transformed into Figure 5, where the relative degree of crystallinity, $X_t$, is presented as a function of crystallization time. Here, $X_t$ is a function of crystallization time which can be defined as follows:

$$X_t = \frac{\int_{t_0}^{t} (dH_c/dt)dt}{\int_{t_0}^{t_\infty} (dH_c/dt)dt}$$

where $t_0$ and $t_\infty$ are the commencement and completion time of crystallization, respectively. As can be seen in Figure 5, it takes less time for crystallization to complete at a higher cooling rate. In addition, all $X_t$ versus $t$ curves are seen to have approximately the same S-shape, indicating that the curves tend to become flat at the later stage due to the spherulite impingement.

The crystallization half-time, $t_{1/2}$, can be estimated from the time at which the extent of crystallization is half completed as seen in Figure 5. Figure 6 shows the crystallization half-times for HPCLs and LPCL at different cooling rates. From Figure 6, it can be seen that $t_{1/2}$ for HPCLs decreases gradually at a specific cooling rate as the length of linear segments increases but as the number of branches decreases. In contrast, $t_{1/2}$ for LPCL shows an intermediate value between HPCL–10 and HPCL–20.

Table 2. Crystallization peak temperature $T_p$, heat of crystallization $\Delta H_c$, and crystallinity $X_c$ of HPCLs and LPCL.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallization parameter</th>
<th>Cooling rate (°C·min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_p$ (°C)</td>
<td>$\Delta H_c$ (J·g$^{-1}$)</td>
</tr>
<tr>
<td></td>
<td>$X_c$ (%)</td>
<td></td>
</tr>
<tr>
<td>HPCL–5</td>
<td>35.2</td>
<td>32.0</td>
</tr>
</tbody>
</table>
|        | 29.6                     | 27.3                          | 25.0
| HPCL–10| 35.4                     | 31.2                          |
|        | 29.4                     | 27.8                          | 25.6
| HPCL–20| 38.7                     | 35.5                          |
|        | 34.1                     | 32.6                          | 31.2
| LPCL   | 36.0                     | 33.2                          |
|        | 31.6                     | 29.6                          | 26.4
| a) Calculated using $\Delta H_c^0 = 136.4$ J·g$^{-1}$ for a 100% crystalline poly(ε-CL).

Figure 3. DSC exothermic curves for HPCLs and LPCL measured at various cooling rates.
Basically, the crystallization of polymers can be seen as a two-step process: (1) the first step is the cooperative movement of polymer chains in a parallel array, and (2) the later step is the crystallization of these ordered chains that occurs as a result of the intermolecular interactions with a concomitant decrease in free energy.[37] As verified in the previous report, the cooperative chain motion in the melt state is faster for HPCLs with shorter linear segments, i.e., HPCL–20 < HPCL–10 < HPCL–5.[26] This indicates that the polymer chains are transferred to the crystal growth front at a faster rate in the first step of crystallization. However, at the second step, a larger number of branches in HPCLs with the shorter segments act as an obstacle in regular chain packing, and consequently, deter crystallization from proceeding effectively.

The faster crystallization of HPCL–20 than LPCL can be explained by the higher chain mobility of the long linear backbone segments of HPCL–20. First, the chain mobility of HPCL–20 is higher than that of LPCL, which can transport the HPCL–20 chain to the growth front more rapidly than the LPCL chain in the first step of crystallization, and second, the linear backbone segments of HPCL–20 are sufficiently long such that the chain regularity of HPCL–20 is as favorable for effective crystallization as LPCL. This implies that the overall crystallization kinetics can be determined by the rate of chain movement to the crystal growth front in the first step of crystallization.

The non-isothermal crystallization kinetics was further analyzed using the Ozawa model equation, which is an extension from the Avrami equation originally applied in the isothermal crystallization to non-isothermal crystallization. In this case, it is assumed that the sample is cooled at a constant cooling rate as follows:[35,38]

\[ X_t = 1 - \exp\left(-\frac{K(T)}{t^m}\right) \]  

Here, \( K(T) \) is the cooling function at temperature \( T \), and \( m \) is the Ozawa exponent which is similar to the Avrami exponent and dependent on the nucleation and growth mechanism. In order to evaluate the Ozawa parameters \([m \text{ and } K(T)]\), the non-isothermal crystallization exotherms of

\[ X_t \text{ versus } T \text{ plots for HPCLs and LPCL at various cooling rates.} \]

\[ X_t \text{ versus } t \text{ plots for HPCLs and LPCL at various cooling rates.} \]
the HPCLs and the LPCL were analyzed using a double-logarithmic form of Equation (5) as follows:

$$\log \left[ \frac{1}{C_0} \ln \left( \frac{1}{C_0} X_t \right) \right] = \log K(T) - m \log \chi$$

Figure 7 shows Ozawa plots of $\log \left[ -\ln(1 - X_t) \right]$ versus $\log \chi$ for HPCLs and LPCL, indicating that the Ozawa equation can be used to analyze the non-isothermal crystallization process, as the Ozawa equation possesses a good linearity. The Ozawa exponent, $m$, and the cooling function, $K(T)$, for HPCLs and LPCL were estimated from the slope and the intercept of the plots, respectively, and summarized in Table 3. The Ozawa exponent values vary between 3.2 and 3.7, showing only a little fluctuation for the different samples and temperatures, whereas the cooling functions are shown to be much influenced by the specific architecture of HPCLs and LPCL as well as crystallization temperatures.

Figure 8 shows the cooling functions of HPCLs and LPCL increasing exponentially at a lower crystallization temperature. This is normal as it is evident that the viscosity increases with decreasing temperature, which makes the transportation of polymer chains to the growth front very difficult. Comparing $K(T)$ variations with $T$ for HPCLs, the increasing trends of the $K(T)$ values with the decrease in temperature accelerates in the order of HPCL–5 < HPCL–10 < HPCL–20. Considering that the cooling function is a function of nucleation and growth rate, the results of

Table 3. Ozawa exponent, $m$ and the cooling function, $K(T)$ of HPCLs and LPCL at various temperatures.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>HPCL–5</th>
<th>HPCL–10</th>
<th>HPCL–20</th>
<th>LPCL</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>$m$</td>
<td>$\log K(T)$</td>
<td>$m$</td>
<td>$\log K(T)$</td>
</tr>
<tr>
<td>36</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<tr>
<td>35</td>
<td>–</td>
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<td>3.6</td>
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<tr>
<td>31</td>
<td>–</td>
<td>–</td>
<td>3.7</td>
<td>1.6</td>
</tr>
<tr>
<td>30</td>
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<td>2.3</td>
<td>3.7</td>
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<td>29</td>
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<td>28</td>
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<td>27</td>
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</tr>
<tr>
<td>26</td>
<td>3.4</td>
<td>2.9</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Figure 8. Cooling functions, $K(T)$’s, for HPCLs and LPCL at various temperatures.

$K(T)$ for the HPCLs indicate that the crystallization of the HPCLs are accelerated with the longer linear segments and fewer number of branches. This might result from the enhanced chain regularity caused by the incorporation of the longer linear backbone segments and the fewer branching points in the HPCL molecules. In addition, the values of $K(T)$ for HPCL–20 are also observed to be higher than that for LPCL at a specific temperature, which indicates that the nucleation and growth rate for HPCL–20 are faster than for LPCL. This observation agrees well with the $t_{1/2}$ result.

From the variation of the crystallization peak temperature, $T_p$, at the cooling rate, $\chi$, during the non-isothermal crystallization process, the activation energy of crystallization, $E_c$, can be derived by the Kissinger method as follows:

$$\frac{d(\ln(\chi/T_p^2))}{d(1/T_p)} = \frac{E_c}{R}$$

where $R$ is the universal gas constant. Figure 9 shows the Kissinger plots of $\ln(\chi/T_p^2)$ versus $1/T_p$ for HPCLs and LPCL. Overall, for HPCLs and LPCL, the Kissinger plots exhibit a relatively good linearity for the range of cooling rates employed. The activation energy of crystallization was estimated from the slopes of the Kissinger plots of the HPCLs and the LPCL, and the results are summarized in Table 1. Here, it is noteworthy that the $E_c$ values estimated are negative because the crystallization process is exothermic. While the $E_c$ values decrease in the order of HPCL–5 > HPCL–10 > HPCL–20, the $E_c$ value for LPCL lies between HPCL–10 and HPCL–20. Acknowledging that the activation energy of crystallization can be interpreted in view of kinetics as the lower $E_c$ value accelerates the crystallization process,[43,44] the $E_c$ values estimated for HPCLs and LPCL coincide well with the kinetics results obtained from the $t_{1/2}$ and $K(T)$ values. The retarded crystallization of HPCLs with the shorter segments and the more branching points might result from the fact that a greater number of frequent branching points deteriorates chain regularity, and thus hinders the regular chain-packing required for crystallization.

**Conclusion**

In this study, the non-isothermal crystallization kinetics of a series of HPCLs were investigated in conjunction with their molecular architectural difference, and were also compared with their linear counterpart, LPCL. Architectural characteristics of HPCLs can be summarized as the lengths of the linear backbone segments of HPCLs are in the increasing order of HPCL–5 < HPCL–10 < HPCL–20 and the numbers of branching points in HPCLs are in a decreasing order of HPCL–5 > HPCL–10 > HPCL–20. Since LPCL consists of one linear chain, the length of the linear segments was the longest and the number of branching points was the smallest among the samples employed in this study.

The non-isothermal crystallizations of HPCLs and LPCL were performed using DSC at various cooling rates ranging from 2 to 10°C·min⁻¹, and their crystallization kinetics were evaluated at crystallization half-times by using Ozawa cooling functions and according to crystallization activation energies. All these parameters indicated that the non-isothermal crystallization rates of HPCLs gradually decreased with an increasing length of linear backbone segments and with a decreasing number of branching points. In contrast, the crystallization rate of LPCL was found to be an intermediate value between HPCL–10 and HPCL–20. These phenomena can be ascribed to the architectural feature as well as chain mobility. As verified from the apparent activation energy of flow, the cooperative chain motion in the melt state was faster for HPCLs with shorter linear segments, which means that the polymer chains can be transported to the crystal growth front more quickly in the first step of the crystallization process. However, a greater number of heterogeneous branches in HPCLs with shorter segments...
may act as an obstacle in regular chain packing, and consequently deter effective overall crystallization. The faster crystallization of HPCL–20 than LPCL can be explained by the long linear backbone segments and the higher chain mobility of HPCL–20 as explained above.

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

[38] T. Ozawa, Polymer 1978, 19, 1142.