Effect of Endgroup Modification on Dynamic Viscoelastic Relaxation and Motion of Hyperbranched Poly(ether ketone)s

JEONGSOO CHOI, JAE WOO CHUNG, SEUNG-HYUN JANG, SEUNG-YEOP KWAK
Department of Materials Science and Engineering, Seoul National University, 599 Gwanak-ro, Gwanak-gu, Seoul 151-744, Korea

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ABSTRACT: Fluoro-terminated hyperbranched poly(ether ketone) (FHPEK) was synthesized and its end groups were modified with alkyl compounds of different chain lengths, i.e., hexyloxy (C6), dodecyloxy (C12), and octadecyloxy, (C18), to produce alkyl-modified HPEKs (HPEK-C6, HPEK-C12, and HPEK-C18, respectively). Master curves were constructed by using the time-temperature superposition principle. The horizontal shift factors, \( \alpha_T \), used for the construction of the master curves were fit using the William-Landel-Ferry (WLF) equation. From the fitting parameters, the apparent activation energy, \( E_a \), was estimated. With increasing alkyl chain length, the \( E_a \) values were found to decrease in the order FHPEK > HPEK-C6 > HPEK-C12, and then increase for HPEK-C18. The average relaxation time, \( \tau_{HN} \), was determined by fitting of the dynamic moduli \( G'(\omega) \) and \( G''(\omega) \) to the empirical Havriliak-Negami equation. Similarly, the \( \tau_{HN} \) values decreased in the order of FHPEK > HPEK-C6 > HPEK-C12, and then increased for HPEK-C18. This indicates that the endgroup modification with short alkyl chains (C6, C12) increased the molecular mobility due to the internal plasticization effect of these alkyl chains. Modification with the longer alkyl chain (C18) retarded the molecular motion through an antiplasticization effect caused by summation of nonpolar hydrophobic interactions between long hydrocarbon chains. ©2008 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 46: 2079–2089, 2008

Keywords: endgroup modification; hyperbranched; poly(ether ketone); relaxation; viscoelastic properties

INTRODUCTION

Hyperbranched polymers (HBPs) have received considerable attention because their highly branched structures are expected to impart unique physical and chemical properties.1–5 HBPs may be considered as irregular analogues of dendrimers which have well-defined and perfectly branched structures. Dendrimers are prepared through divergent or convergent approaches that follow step-by-step syntheses; HBPs are prepared by direct one-pot polymerization of \( AB_x \)-type monomers.6 This synthetic simplicity, in addition to similar physical/mechanical properties of both HBPs and dendrimers that possess the same repeating units,7 has encouraged many researchers to develop tailor-made materials for specific applications where high performance and/or novel
functionality are needed. For example, HBPs possess highly branched architectures, numerous end group functionalities, and few chain entanglements, which in turn improve solubility, enhance compatibility with other polymers, and reduce melt viscosity.\textsuperscript{7–11} HBPs can be subject to a wide range of structural fine-tuning by adjustment of the degree of branching and/or by modification of numerous endgroups, which play a significant role in determining the dynamic mechanical/rheological properties.\textsuperscript{10,12,13} Furthermore, HBPs have somewhat broader molecular weight distributions than linear polymers and do not exhibit the same dependence of viscosity on the molecular weight; the increase in the viscosity with molecular weight is less than for the corresponding linear analogues.\textsuperscript{3,14} In this regard, along with the possible modification of interaction between numerous functional endgroups, HBPs are expected to be easily processable at higher molecular weights and thus could be very useful as high solids content organic coating agents and polymer rheology control agents/processing aids.\textsuperscript{15,16}

It has been reported, however, that the compactly packed periphery and lack of chain entanglements of HBPs, resulting from the highly branched architecture, produces materials with mechanical brittleness.\textsuperscript{17} This critical drawback limits the practical scope of their technological applications. Several strategies to avoid brittleness have been attempted without sacrificing the HBP architecture. One such example is introducing oligomeric linear segments in the repeating building blocks in HBPs from the AB\textsubscript{x} type macromonomers.\textsuperscript{18} However, this synthetic pathway possesses inherent limits in growing HBPs with multiple branches due to the extremely bulky building units. Another approach is making dendritic-linear di-/triblock copolymers.\textsuperscript{19} In this case, either statistical reaction of both dendritic and linear building blocks or hardly controllable growth of dendritic blocks from the linear chain ends limits its practical accessibility. One possible alternative possessing synthetic advantage over the other methods is endgroup modification with short chains capable of imparting flexibility, such as alkyl chains.

In this study, we present results on the modification of hyperbranched poly(ether ketone)s (HPEKs) based on 3,5-difluoro-4'-hydroxy-benzophenone. The modification was carried out with alcohols of different chain lengths, specifically, hexyl alcohol, dodecyl alcohol, and octadecyl alcohol. The objective of this study was to elucidate the effect of alkyl chain modification on the various thermophysical properties.

**EXPERIMENTAL**

\textsuperscript{1}H NMR spectra were obtained with CDCl\textsubscript{3} solutions using a Varian VXR 200 (200 MHz for \textsuperscript{1}H) spectrometer with tetramethylsilane as an internal standard. Fourier-transform infrared spectroscopic analysis (FT-IR) was carried out using a Perkin-Elmer spectrometer as thin films on KBr plates. \textsuperscript{19}F NMR spectra were obtained with dimethyl sulfoxide-d\textsubscript{6} solutions using a Bruker AM 200 spectrometer (188.1 MHz for \textsuperscript{19}F) with FCl\textsubscript{3} as an external standard.

Gel permeation chromatography (GPC) was carried out on a Waters chromatograph connected to a Waters 410 differential refractometer. Three styragel columns connected in series were used with chloroform as the solvent. The $M_\text{n}$ and $M_\text{w}/M_\text{n}$ values were calculated from the resulting GPC data based on calibration with polystyrene standards of known molecular weights and polydispersity indexes.

Glass transition temperatures, $T_\text{g}$'s, were measured using differential scanning calorimetry (DSC) on a TA Instruments DSC2920 differential scanning calorimeter. Heating rates were 10 °C min\textsuperscript{-1}, and $T_\text{g}$ was taken as the midpoint of the inflection tangent, upon the second heating scan.

**Synthesis**

**Preparation of Fluoro-Terminated Hyperbranched Poly(ether ketone) (FHPEK, 3)**

3,5-Difluoro-4'-hydroxy-benzophenone (2), used for the preparation of the corresponding fluoro-terminated hyperbranched poly(ether ketone) FHPEK, was synthesized according to the reaction pathway first developed by Hawker et al. (Scheme 1). The structural verification of these compounds has been described elsewhere.\textsuperscript{20,21}

**Preparation of Hexyloxy-Terminated Hyperbranched Poly(ether ketone) (HPEK-C6, 4)**

FHPEK (2 g) was dissolved in dry N-methylpyrrolidone (25 mL), and hexyl alcohol (7.34 g, 72.2 mmol), potassium carbonate (4.6 g, 40 mmol), and dry toluene were added. The reaction mixture was then heated at reflux under nitrogen for 3 h, with the water being collected in a Dean-Stark trap. The distillate was collected and removed.
until the temperature of the reaction mixture had reached $\sim 150^\circ C$. Stirring and heating was then continued for another 8 h to complete the reaction. The mixture was poured into 500 mL of water, and the precipitate was collected by filtration and washed thoroughly with methanol (2 × 500 mL) to remove unreacted low molecular impurities. Yield: 80%; IR (KBr) 3000, 1660, 1580, 1500, 1430, 1300, 1230 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 0.87 (s, 3H, $-CH_3$), 1.25 (s, 4H, $-(CH_2)_2$), 1.43 (s, 2H, $-CH_2$), 1.77 (s, 2H, $-CH_2$), 6.80–7.24 (complex m, 5H), 7.73 (br s, 2H).

**Preparation of Dodecyloxy-Terminated Hyperbranched Poly(ether ketone) (HPEK-C12, 5)***

The reaction procedure was identical to that of HPEK-C12 except dodecyl alcohol (12.454 g, 47.9 mmol) was used instead of dodecyl alcohol. Yield: 82%; IR (KBr) 3000, 1660, 1580, 1500, 1430, 1300, 1230 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 0.87 (s, 3H, $-CH_3$), 1.25 (s, 28H, $-(CH_2)_{14}$), 1.43 (s, 2H, $-CH_2$), 1.77 (s, 2H, $-CH_2$), 4.04 (s, 2H, $-O-CH_2$), 6.80–7.24 (complex m, 5H), 7.73 (br s, 2H).

**Preparation of Octadecyloxy-Terminated Hyperbranched Poly(ether ketone) (HPEK-C18, 6)***

The reaction procedure was identical to that of HPEK-C12 except octadecyl alcohol (12.454 g, 47.9 mmol) was used instead of dodecyl alcohol. Yield: 88%; IR (KBr) 3000, 1660, 1580, 1500, 1430, 1300, 1230 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 0.87 (s, 3H, $-CH_3$), 1.25 (s, 28H, $-(CH_2)_{14}$), 1.43 (s, 2H, $-CH_2$), 1.77 (s, 2H, $-CH_2$), 4.04 (s, 2H, $-O-CH_2$), 6.80–7.24 (complex m, 5H), 7.73 (br s, 2H).

**Frequency Sweep Dynamic Mechanical Measurements***

The dynamic mechanical properties of FHPEK, HPEK-C6, HPEK-C12, and HPEK-C18 were measured with the Rheometrics RMS-800 mechanical spectrometer.

The measurements were performed in dynamic shear oscillatory mode using a 25-mm diameter parallel disc geometry with a gap setting of about 2 mm. The range of angular frequency was from 0.1 to 100 rad s$^{-1}$ and temperature was selected from the range of 120–232 $^\circ C$, depending on the sample. Individual samples were tested isothermally with parallel-plate geometry under a thermally regulated nitrogen atmosphere. The lowest temperature of the measurements was limited by the slippage between the sample and the disk; the highest temperature was limited by thermal degradation. A strain amplitude of 2% was selected to be large enough for accurate torque signals but small enough to keep the material response in the linear region. The linear viscoelastic (LVE) region was determined by dynamic strain sweep tests.

**RESULTS AND DISCUSSION***

**Synthesis and Characterization***

The monomer 3,5-difluoro-4-0-hydroxybenzophene and fluoro-terminated hyperbranched poly(ether ketone) FHPEK were synthesized according to a reaction first developed by Hawker and Chu$^{20}$ as modified in our previous report$^{21}$ to achieve the multigram yields required for dynamic mechanical measurements. The numerous fluorine functionalities in the chain-ends of
FHPEK are capable of further modification by simple nucleophilic substitution. As shown in Scheme 1, the different alkyl chains were introduced in the chain-ends of FHPEK by using primary alcohols to produce HPEK-C6, HPEK-C12, and HPEK-C18. Since there are no alkyl protons in FHPEK before the substitution reaction, $^1$H NMR is an effective way to monitor this reaction. For example, the $^1$H NMR spectrum of HPEK-C18 clearly shows the alkyl proton peaks in the range from 0.8 to 4 ppm (Fig. 1). As indicated in the peak assignments in Experimental section, the FT-IR spectra of FHPEK, HPEK-C6, HPEK-C12, and HPEK-C18 also show that the alkyl modifications of FHPEK were successful and did not induce significant changes in other chemical structures.

Molecular weights and polydispersity indexes of FHPEK and alkyl-modified HPEKs were determined using GPC analysis calibrated with linear polystyrene standards, and are listed in Table 1. HBPs are generally expected to exhibit a lower molecular weight in comparison to their linear analogues. This is mainly ascribed to HBPs having a smaller hydrodynamic volume due to their branched structures, compared to their linear counterparts of the same molecular weight and chemistry. In addition, the deviation of molecular weight of HBP measure by GPC from absolute values is known to be related with the degree of branching; the higher the degree of branching, the larger the deviation from absolute values. Since the degree of branching of FHPEK and alkyl-modified HPEKs of this study is identical, the deviations of absolute molecular weights of the samples of this study is thought to be not much different from the values listed in Table 1.

As shown in Table 1, the molecular weights increase with the introduction of the alkyl chains. The increase in polydispersity indexes of the HPEKs compared to that of FHPEK is ascribed to the statistical substitution of alkyl chains. In addition, the difference in polydispersity indexes among alkyl-modified HPEKs is ascribed to the different distributions of degree of substitution with each alkyl chain.

Differential scanning calorimetry (DSC) was used to characterize the effect of alkyl modification on the thermal transitions of FHPEK. As also shown in Table 1, the glass transition temperature, $T_g$, decreased with the introduction of longer alkyl-chains but it increased again for HPEK-C18, i.e., FHPEK > HPEK-C6 > HPEK-C12 < HPEK-C18. The significant decrease in $T_g$ on introduction of short alkyl chains (C6, C12) is ascribed to a reduction in the intermolecular interaction induced by disturbing the polar interaction in FHPEK and/or transforming the relatively strong polar interaction into a weak nonpolar hydrophobic interaction. On the other hand, the slight increase in $T_g$ for HPEK-C18 may result in the increase in the sum of these weak interactions.

![Figure 1](https://example.com/figure1.png)

Figure 1. Aliphatic partitions of the $^1$H NMR spectrum of HPEK-C18 in CDCl$_3$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$ (a)</th>
<th>$M_w$ (b)</th>
<th>$M_w/M_n$ (c)</th>
<th>$T_g$ (°C) (d)</th>
<th>DB (e)</th>
<th>DS (f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FHPEK</td>
<td>10,600</td>
<td>25,400</td>
<td>2.4</td>
<td>145</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>HPEK-C6</td>
<td>15,700</td>
<td>51,300</td>
<td>3.3</td>
<td>100</td>
<td>0.65</td>
<td>0.76</td>
</tr>
<tr>
<td>HPEK-C12</td>
<td>18,700</td>
<td>97,800</td>
<td>5.2</td>
<td>94</td>
<td>0.65</td>
<td>0.80</td>
</tr>
<tr>
<td>HPEK-C18</td>
<td>25,000</td>
<td>57,600</td>
<td>2.3</td>
<td>107</td>
<td>0.65</td>
<td>0.84</td>
</tr>
</tbody>
</table>

(a) Number-average molecular weight determined by GPC.
(b) Weight-average molecular weight determined by GPC.
(c) Polydispersity index.
(d) Glass transition temperature observed on second heating.
(e) Degree of branching.
(f) Degree of substitution.

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nonpolar hydrophobic interactions and thus partial crystallization between long C18 chains. There have been studies about the effect of alkyl modification on the thermal properties and crystallization behaviors of HBPs, though it is not the main focus of this study, reporting a similar tendency with our result. Voit and coworkers reported the alkyl-modified aromatic hyperbranched polyester had its $T_g$ minimum at C12 and the melting transitions of these alkyl chains were observed for C14 and longer. Hult and coworkers reported a more pronounced tendency to alkyl chain crystallization of alkyl-modified all-aliphatic hyperbranched polyester with its $T_g$ minimum at C6 chains. It should be also noted that the relatively broad polydispersity index might affect the glass transition of HPEK-C12, though it should be minimal. One of most important aspects of polydispersity in affecting glass transition would be whether or not there remain the low molecular weight impurities in the sample because they might act as a plasticizer with lowering $T_g$. In this study, there wouldn't be any low molecular weight impurities other than the unreacted alcohols since the alcohols are not reactive each other in the given reaction conditions. Moreover, the product mixtures were all thoroughly washed out several times with MeOH to completely remove the unreacted alcohols.

Another important material characteristic to describe the structural features of HBPs is the degree of branching (DB). Unlike dendrimers, which are perfectly branched and have a DB of 100%, HBPs inherently possess a certain degree of imperfection. Therefore, their DB values can be anywhere between 0 and 100%. Statistical polymerization reaction of ideal AB$_2$-type monomer results in a DB of 50%, assuming that both B functional groups are of equal reactivity, independent of structure and location. The DB of a HBP is commonly calculated according to the following equation:

$$DB = \frac{D + T}{D + L + T}$$ (1)

where, $D$, $T$, and $L$ are the fractions of dendritically, terminally, and linearly incorporated monomer units in the HBP. For high molecular weights, the sum of terminal and dendritic units becomes effectively identical since the number of dendritic units is theoretically equal to that of terminal units plus one. Thus, eq. 1 can be simplified to:

$$DB = \frac{2T}{L + 2T}$$ (2)

FHPEK includes a terminal unit with two fluorine groups and a linear unit with one fluorine group. The different chemical environments of terminal and linear fluorine groups in FHPEK allow the relative proportion to be evaluated by $^{19}$F NMR spectroscopy. As indicated in Figure 2(a), the resonance peak at $-108.38$ ppm can be assigned to the terminal unit and the peak at $-108.83$ ppm to the linear unit. The DB value of FHPEK was determined using the relative percentage of terminal and linear units obtained from integration of the respective signals of the $^{19}$F NMR spectra (also see Table 1). It is true that direct determination of DB values by $^{19}$F NMR is impossible for alkyl-modified HPEKs due to the change or loss of fluorine peaks upon the substitution reaction. However, since no significant change in chain architecture occurs during the alkyl-substitution reaction, it is reasonable to consider the DBs of HPEK-C6, HPEK-C12, and HPEK-C18 as being identical to that of FHPEK.
19F NMR spectra were also used to characterize the degree of substitution of chain-ends of FHPEK into alkyl groups. Figure 2(b) shows the 19F NMR spectrum of HPEK-C18. In comparison with the spectrum of FHPEK shown in Figure 2(a), the peak in the HPEK-C18 spectrum must be from the residual fluorine groups that have not been substituted. Thus, the degree of substitution, DS, can be calculated from the decrease in the relative integration of the fluorine peaks:

\[
DS = 1 - \frac{I(\text{HPEK} - \text{C}_x)}{I(\text{FHPEK})}
\]  

where, \(I(\text{FHPEK})\) is the total integration of fluorine peaks for FHPEK and \(I(\text{HPEK} - \text{C}_x)\) is that for HPEK-C6, HPEK-C12, or HPEK-C18. As also seen in the spectra in Figure 2, the peak for the terminal units of FHPEK disappeared after the alkyl substitution whereas that for the linear units remained. The disappearance of the terminal units can be the result of dissubstitution or at least monosubstitution of the terminal fluorine groups. The resulting DSs are determined to range from 0.76 to 0.84 without correlation with the length of substituted alkyl chains as listed in Table 1.

**Dynamic Mechanical Relaxation Behavior**

Figure 3 shows the logarithmic plots of the shear loss modulus, \(G''(\omega)\), versus the shear storage modulus, \(G'(\omega)\), both taken at the same frequency \(\omega\) for FHPEK and the three HPEKs at various temperatures. In general, the \(G''(\omega)\) versus \(G'(\omega)\) plots have been used for investigating the effects of temperature, molecular weight, and its distribution, branching architecture, and the phase structure of the polymers on the viscoelastic behavior of bulk polymers. For example, it has been reported that the \(G''(\omega)\) versus \(G'(\omega)\) curves shifted to the \(G'(\omega)\) region, where elastic response is dominant, as the molecular weight and/or the length of branching increased and thus favorable inter- and/or intrachain interaction increased.\(^{29-33}\)

In Figure 3, \(G''(\omega)\) versus \(G'(\omega)\) curves for alkyl-modified HPEKs are positioned at the upper-left side of the Figure, showing viscous response dominant features for these samples. Recognizing that the molecular weights of alkyl-modified HPEKs were slightly higher than those of FHPEK, the deviation of the \(G''(\omega)\) versus \(G'(\omega)\) curves of alkyl-modified HPEKs is ascribed mainly to the substitution of strongly interacting polar end groups with weakly interacting nonpolar hydrophobic alkyl chains. This is in accordance with the glass transition temperature results.

Another merit of the \(G''(\omega)\) versus \(G'(\omega)\) plot is that it provides a critical examination of the applicability of the superposition principle with respect to time-temperature correspondence. In the linear viscoelastic region, assuming that no changes are made to the structure within the assumed temperature range, the \(G''(\omega)\) or \(G'(\omega)\) versus \(\omega\) plots at different temperatures can be superimposed to form a master curve. It is noteworthy that the \(G''(\omega)\) versus \(G'(\omega)\) data for all FHPEK and alkyl-modified HPEKs at varying temperatures fall on one curve as shown in Figure 3, which means that the time-temperature superposition principle is applicable for these samples. The results for a case in which the time-temperature superposition principle was applied are shown in Figures 4-7 in the form of moduli \((G', G'')\) versus reduced frequency \((\alpha_T\omega)\) for FHPEK, HPEK-C6, HPEK-C12, and HPEK-C18, respectively. The vertical shift for construction of master curves was assumed to be negligible, and the same horizontal shift factor, \(\alpha_T\), was used for shifting both \(G'(\omega)\) and \(G''(\omega)\) curves along the frequency axis with respect to the reference curve at \(T_g = 50^\circ C\).

As shown in Figure 4, the rubbery plateau region is seen with an intersection between \(G'(\omega)\) and \(G''(\omega)\) for FHPEK. In contrast, no rubbery plateau region is seen for alkyl-modified HPEKs.

[Image 68x553 to 292x725]
and viscous behavior dominates over the experimental temperature range (Figures 5–7). Furthermore, the shear storage modulus, $G'$, is found to greatly decrease as endgroups are substituted with alkyl chains.

Figure 8 shows plots of the horizontal shift factor, $a_T$, of FHPEK and HPEK-C6, HPEK-C12, and HPEK-C18 as a function of temperature. The solid lines are the results of nonlinear curve fitting to the William-Landel-Ferry (WLF) equation:

$$\log a_T = -\frac{C_1(T - T_0)}{C_2 + (T - T_0)}$$  \hspace{1cm} (4)

where, $C_1$ and $C_2$ are constants, and $T_0$ is the reference temperature. The $T_0$ value of each HBP was fixed at $T_g + 50$ °C to remove the additional horizontal shifts due to the change of $T_0$ according to samples. The $C_1$ and $C_2$ were calculated from the nonlinear curve fitting of an experimentally determined $a_T$ using the WLF equation and the results are listed in Table 2. The fitting was accomplished utilizing a specialized script.
running under Origin software (version 6.0, Microcal Software), which calls the Levenburg-Marquet minimization routine to provide the best-fit parameters compared to the data sets.

The fitting results were further analyzed to extract the apparent activation energy for viscoelastic relaxation, which can be calculated formally as:

$$\Delta E_a = R \left( \frac{d \ln \alpha_T}{d T^{-1}} \right) = 2.303 R \left( \frac{C_1 C_2 T^2}{C_2 + T - T_0} \right)$$

(5)

In general, the apparent activation energies tend to decrease with increasing temperature, indicating that segmental sliding is the major mode of molecular motion above the glass transition temperature. This sliding motion requires cooperative motion of larger segments of the main chain. Figure 9 shows the apparent activation energies as a function of reduced temperature ($T - T_0$). As shown in Figure 9, the temperature dependency is not different over all FHPEK and alkyl-modified HPEKs, showing decreasing tendency of activation energies with increasing temperature. However, at each reduced temperature, it is evident that the apparent activation energy of FHPEK is larger than that of the alkyl-modified HPEKs. This is ascribed to the increase in

Table 2. Nonlinear Curve Fitting for Hyperbranched Poly(ether ketone)s to the WLF Equation

<table>
<thead>
<tr>
<th>Sample</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$T_0$ a</th>
</tr>
</thead>
<tbody>
<tr>
<td>FHPEK</td>
<td>5.6</td>
<td>98</td>
<td>196</td>
</tr>
<tr>
<td>HPEK-C6</td>
<td>5.1</td>
<td>97</td>
<td>150</td>
</tr>
<tr>
<td>HPEK-C12</td>
<td>4.8</td>
<td>83</td>
<td>144</td>
</tr>
<tr>
<td>HPEK-C18</td>
<td>5.8</td>
<td>101</td>
<td>157</td>
</tr>
</tbody>
</table>

*Reference temperature $T_g + 50$ °C.
free volume by substituting polar chain-ends of FHPEK into a nonpolar hydrophobic alkyl chains, acting as internal plasticizers. The segmental sliding motion is facilitated with the increased free volume in alkyl-modified HPEKs, which results in the lower activation energies. Among the alkyl-modified HPEKs, the apparent activation energy increases in the order of HPEK-C12 < HPEK-C6 < HPEK-C18, indicating that the increase in free volume reached its maximum with C12 alkyl chains. This is in good accordance with the glass transition data in the previous section, showing its $T_g$ minimum at C12 chains. On the other hand, the repetitive long alkyl-chains of C18 may increase the sum of hydrophobic interactions, which results in the constrained segmental sliding motions with higher activation energy.

Average Relaxation Time and Molecular Mobility

Both the dynamic moduli, $G'(\omega)$ and $G''(\omega)$, of FHPEK and HPEK-C6, HPEK-C12, and HPEK-C18 as a function of temperature can be used to obtain a quantitative measure of their corresponding molecular mobility, and to evaluate their structural changes in terms of the molecular
mobility. It is well-known that the relaxation behavior of a polymer system follows an exponential relaxation process not only with a single relaxation time but with a distribution of relaxation times. Thus, the dynamic mechanical data must be treated with empirical fitting functions to represent the relaxation behavior and determine the single average relaxation times. One such empirical fitting function that has achieved widespread acceptance is the Havriliak-Negami (HN) distribution function of relaxation times. The HN function was originally derived to fit dielectric relaxation data, and can also be used to analyze dynamic mechanical relaxation data by appropriately changing the variables from dielectric to dynamic mechanical variables, considering the general relationships between them. The empirical HN equation is given by

$$G^* = G' + iG'' = G_\infty + \frac{G_0 - G_\infty}{1 + (i\omega \tau_{HN})^{\gamma}}$$

where, $G^*(\omega)$ is the complex shear modulus, $G_\infty$ and $G_0$ are the unrelaxed and relaxed modulus, respectively, $\tau_{HN}$ is the characteristic relaxation time, and $\alpha$ and $\beta$ are shape parameters ranging between 0 and 1 that account for the symmetric and asymmetric relaxation time distribution, respectively. Considering the real and imaginary parts of $G^*(\omega)$, the storage and loss moduli can be derived as

$$G'(\omega) = G_\infty + (G_0 - G_\infty) \times \frac{\cos(\beta \theta)}{[1 + 2(\omega \tau_{HN})^2 \cos(\pi \alpha / 2) + (\omega \tau_{HN})^{2\gamma \beta / 2}]}$$

$$G''(\omega) = (G_\infty - G_0) \times \frac{\sin(\beta \theta)}{[1 + 2(\omega \tau_{HN})^2 \cos(\pi \alpha / 2) + (\omega \tau_{HN})^{2\gamma \beta / 2}]}$$

with

$$\theta = \arctan \left( \frac{(\omega \tau_{HN})^2 \sin(\pi \alpha / 2)}{1 + (\omega \tau_{HN})^2 \cos(\pi \alpha / 2)} \right)$$

The average relaxation times, $\tau_{HN}$, of FHPEK and HPEK-C6, HPEK-C12, and HPEK-C18 as a function of temperature are shown in Figure 10. After alkyl modification, $\tau_{HN}$ decreases and hence, the molecular mobility increases. Similar to the activation energy results, the average relaxation time of the HPEKs increases in the order HPEK-C12 < HPEK-C6 < HPEK-C18. These findings indicate that the free volume increases on substitution of alkyl chains up to C12 as schematically represented in Figure 11. In contrary, the substitution with the longer C18 chains did not increase the free volume further but did retard molecular motion. As represented in Figure 11, the retarded molecular motion in HPEK-C18 can be explained by an antiplasticization effect caused by substituted alkyl chains that are long enough to give rise to increase in sum of hydrophobic interactions restricting segmental motions. Specifically, although the interaction between individual nonpolar hydrocarbons is negligible, the summation of such intermolecular interactions becomes significant as longer alkyl (C18) chains are introduced in the chain ends. These stronger interactions in HPEK-C18 retard segmental sliding motions and thus decrease the overall molecular mobility compared to that of HPEKs with shorter alkyl (C6, C12) chains.

**CONCLUSIONS**

In the present work, FHPEK was modified with linear alcohols of different chain length. The degree of branching for FHPEK was determined to be 0.65 and the degrees of substitution of the alkyl-modified hyperbranched poly(ether ketones)s HPEK-C6, HPEK-C12, and HPEK-C18 were estimated to be 0.76, 0.80, and 0.84, respectively. The glass transition temperature, $T_g$, was reduced by modification with alkyl chains at the endgroups, although HPEK-C18 showed a slightly higher $T_g$ than that of HPEK-C12. This effect is ascribed to an increase in free volume as flexible alkyl chain ends are introduced.

From the $G''(\omega)$ versus $G'(\omega)$ curves, it was predicted that the time-temperature superposition principle was applicable. The curves showed features indicating that viscous response dominates for these samples. Recognizing that the molecular weights of the alkyl-modified HPEKs are slightly higher than those of FHPEK, the deviation of the $G''(\omega)$ versus $G'(\omega)$ curves of the alkyl-modified HPEKs is mainly ascribed to the substitution of strongly interacting polar endgroups with weakly interacting nonpolar hydrophobic alkyl chains.

From the parameters obtained by nonlinear curve fitting of the horizontal shift factor, $\alpha_T$, to the WLF equation, the apparent activation energy $E_a$ was estimated for the corresponding temperatures. The activation energies of the alkyl-modified HPEKs were smaller than that of FHPEK.
and were shown to increase in the order HPEK-C12 < HPEK-C6 < HPEK-C18. The average relaxation times, $\tau_{HN}$, of the alkyl-modified HPEKs were shorter than that of FHPEK and in the order HPEK-C12 < HPEK-C6 < HPEK-C18. The observation of lower activation energies for the alkyl-modified HPEKs than for FHPEK is ascribed to the increase in free volume resulting from the substituted alkyl chains, which act as an internal plasticizer. As a result of antiplasticization of the longer alkyl chains (C18), the molecular mobility was decreased for HPEK-C18, which shows a higher activation energy than that of HPEK-C6 and HPEK-C12.

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REFERENCES AND NOTES