Molecular Relaxation and Local Motion of Hyperbranched Poly(ether ketone)s with Reference to Their Linear Counterpart. 1. Effect of Degrees of Branching

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ABSTRACT: Three different fluoro-terminated hyperbranched poly(ether ketone)s (FHBPEKs) with variable degrees of branching and their linear analogous poly(ether ketone) (LPEK) whose chemical structure and molecular weight were similar to those of the FHBPEKs were synthesized. Cyano-terminated hyperbranched poly(ether ketone), CHBPEK, in which the terminal groups of FHBPEK were modified with cyanophenol was also prepared as a reference. The local relaxation and motion of the three FHBPEKs, in conjunction with their hyperbranched structure and the degrees of branching, were characterized by the solid-state ^{1}H pulsed wide-line NMR spectroscopy and compared to that of the linear counterpart, LPEK. From the measurements of the spin−lattice relaxation times in the rotating frame, $T_{1\rho}$'s, over the temperature range 140−400 K, the correlation times, τ_c's, and the corresponding activation energies, E_a's, were determined, providing a direct evaluation for the local molecular motion. FHBPEKs were found to be structurally heterogeneous because they had two different motions throughout the system; with aid of the τ_c results of CHBPEK, each was assigned as originating from the linear and from the terminal/branched portion, respectively. In contrast, LPEK exhibited single relaxational and motional behavior, indicating that it was structurally homogeneous. The molecular mobility of the linear portion of FHBPEKs was higher than that of LPEK and enhanced with increasing degree of branching in the entire range of experimental temperatures. For the terminal/branched portion of the FHBPEKs, the local mobility was little affected by the degree of branching, especially at the temperature range from 140 K to room temperature, but increased afterward as was for the linear portion.

Introduction

Recently, it has become essential in many areas to tailor-fit a polymeric material more accurately for a specific application where high performance or a novel function is needed. This can be achieved with design of the new architecture realizing large production at a low cost and the precise control of the polymer structure. A good example is the hyperbranched polymers (HBPs) which are prepared by one-step polymerization of AB_2-type monomers, thereby resulting in a branching greater than ca. 50% and a semiglobular shape with high number of end groups.[1,2] These polymers have been shown to possess very unique physical properties and many new application potentials in comparison to the linear polymers.[3] For example, enhanced solubility and reduced melt viscosity promise the use of HBPs as a new class of organic coating agents and polymer rheology modifiers/processing aids.[4−6] High end group functionality provides an effective means to increase and control the intermolecular interaction and miscibility with other polymers, producing the novel polymer blends.[7] Furthermore, HBPs offer a fine structural tunability by controlling the degree of branching and/or modification of the end group functionality, which play an important role in determining the final physical/mechanical properties. Recently, studies have attempted to correlate the hyperbranched structures with the various physical properties.[8,9] However, general factors characterizing and explaining the effect of the hyperbranched structure on the unique physical properties are not well understood. One such factor is the molec-

ular mobility in the solid state, which acts as a bridge to connect the structure−property relationships since the mobility is inevitably interdependent with structure and strongly governs the physical/mechanical properties in the end use. Despite its importance, however, little has been done to study the molecular motions of HBPs with controlled degrees of branching and/or with various end groups and compare them to their linear analogue.

Solid-state nuclear magnetic resonance (NMR) spectroscopy has been used for polymers over a wide range of length scales.[10] This technique has also proved useful for the study of multiphase solid polymers because polymers in different environments have different molecular dynamics and different NMR relaxation times.[11] Thus, the measurement of such relaxation rates has also greatly contributed to our understanding of molecular dynamics of polymers. The probability of success in quantitatively determining significant differences in molecular mobility of the whole polymer system will depend on the exact choice of experimental NMR protocols used. The motional frequencies to which NMR can be sensitive cover a wide range, from ≤ 1 to $> 10^{10}$ Hz, and are selectable within broad limits by the user. The strength and the characteristic frequency of the interaction being modulated by the motion govern the selectivity of a particular NMR experiment. In some cases, relationships can be derived by directly relating NMR parameters to the actual frequencies of bond rotations in polymers or bond rotations and overall molecular tumbling for small molecules. With high-resolution solid-state NMR, motional phenomena can be probed at all spectroscopically resolved sites in the molecules.[12] This allows independent characterization

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of the primary backbone motions in the presence of the motion of the side chains and end groups; however, it requires much time and efforts to analyze the molecular motion. On the other hand, the pulsed wide-line method can provide a convenient way to get information about average local motion in a whole polymeric system.[13] We denote all so-called rotating frame spin−lattice relaxation time experiments by the symbol $T_{1\rho}$. They are generally most sensitive to motions in the tens of kilohertz to a few hundred kilohertz range.[14] However, we cannot determine the molecular mobility solely from the $T_{1\rho}$ values and have to convert the $T_{1\rho}$ data to the correlation time, τ_c, based on Bloembergen−Purcell−Pound (BPP)[15] and Kubo−Tomita (KT)[16] theory. The correlation time, τ_c, is defined as the average time required for motional events and commonly expresses the molecular mobility of polymers. It is worth noting that according to BPP/KT theory τ_c decreases as the motion gets faster and hence the mobility increases.

In the present paper, fluoro-terminated hyperbranched poly(ether ketone) (FHBPEK) and the corresponding linear analogue, poly(ether ketone) (LPEK), of the FHBPEK were synthesized. Also prepared were cyano-terminated hyperbranched poly(ether ketone) (CHBPEK) in order to confirm the NMR analyses of the relaxation and motion for the FHBPEK, in which the terminal fluorine of the FHBPEK was modified with cyanophenol. In addition, FHBPEKs with different degrees of branching were prepared to investigate the effect of degree of branching on the relaxation and motion, referred to as FHBPEK-CM01 and -CM02. The degree of branching was controlled and varied by introducing core molecules (1.9 mol % for FHBPEK-CM01 and 3.4 mol % for FHBPEK-CM02) in the synthesis procedure to the extent of not varying the number-average molecular weights significantly among the resulting three FHBPEKs. The objectives of this paper are mainly concerned with elucidating the local molecular motions of the four HBPs and an LPEK by ^{1}H solid-state NMR spectroscopy with respect to the difference between hyperbranched and linear structures as well as the degrees of branching.

Experimental Section

General Characterization. Infrared spectra were recorded on a Perkin-Elmer spectrometer as thin film on KBr. ^{1}H NMR spectra were obtained on a Varian VXR-200 (200 MHz for ^{1}H) spectrometer with the TMS proton signal as the internal standard. ^{19}F NMR spectra were recorded on solution DMSO-d_6 on a Varian VXR-200 spectrometer (188.1 MHz for ^{19}F) with external CFCl$_3$ as the standard. Gel permeation chromatography (GPC) was conducted on a Waters 600 with a Waters 410 differential refractometer, Waters 600 pump, and controller; data analysis was performed by Autochro GPC software. Two styragel columns connected in series were used with THF as solvent. The M_n and M_w/M_n values were calculated from the GPC results based upon calibration with the polystyrene standard of the known molecular weight and polydispersity index. Glass transition temperatures (T_g's) were measured by differential scanning calorimetry (DSC) on a Perkin-Elmer DSC 7 differential scanning calorimeter. Heating rates were 20 °C/min, and T_g was taken as the midpoint of the inflection tangent, upon the second heating scan.

Synthesis. 3,5-Difluoro-4′-hydroxybenzophenone, **2**, used for the preparation of the corresponding hyperbranched poly-(ether ketone) (FHBPEK), **3**, was synthesized according to the reaction developed by Hawker (Scheme 1). The structural verification of **2** and **3** has been described elsewhere.[17]

Core Molecule, 4. To a mixture of fluorobenzene (4.5 g, 46.8 mmol) and aluminum chloride (6.7 g, 50 mmol) in dry 1,2-dichloroethane (20 mL) was added dropwise 1,3,5-benzenetricarbonyl trichloride (5 g, 18.8 mmol) in 1,2-dichloroethane (10 mL). The reaction mixture was stirred at room temperature under argon for 4 h. Water (15 mL) was added, and stirring continued overnight. The reaction mixture was then poured into water (300 mL) and extracted with methylene chloride (3 × 100 mL). The combined extracts were dried and evaporated to dryness. The crude product was recrystallized in methanol to give the benzophenone, **4**, as a white solid: 71%, mp 102−103 °C. IR: 3000, 1690, 1600, 1210, 830 cm^{-1}. ^{1}H NMR (dimethyl sulfoxide-d_6): δ 8.24 (s, 1 H, ArH), 7.96 (complex d, 6 H, $J = 6$ Hz, ArH), 7.46 (complex t, 6 H, $J = 9$ Hz, ArH).

Preparation of Fluoro-Terminated Hyperbranched Poly(ether ketone)s Having Core Moiety (FHBPEK-CMs), 5. Two FHBPEK-CMs were prepared from **2** (3 g, 12.8 mmol) and **4** (0.10 g, 0.225 mmol and 0.20 g, 0.45 mmol) using a procedure similar to that of the preparation of **3**. This results in the hyperbranched poly(ether ketone), **5**, having different degree of branching as a white solid; 90−94%. IR: 1670, 1590, 1500, 1430, 1340, 1230 cm^{-1}.

Preparation of Linear Poly(ether ketone) (LPEK), 6. A mixture of 4,4′-difluorobenzophenone (2.0 g, 9.2 mmol), resorcinol (1.0 g, 9.2 mmol), dry *N*-methylpyrrolidone (20 mL), and potassium carbonate (2.8 g) were heated at 200 °C under argon for 3 h. The reaction mixture was poured into water (800 mL), and the precipitate was collected and washed with methanol (500 mL × 2). This gave the linear poly(ether ketone), **6**, as a white solid; 95%. IR: 1680, 1580, 1500, 1480, 1300, 1270 cm^{-1}.

Preparation of Cyano-Terminated Hyperbranched Poly(ether ketone), 7. A mixture of **3** (2 g), 4-cyanophenol (2 g, 16.8 mmol), potassium carbonate (2.8 g), and *N*-methylpyrrolidone (20 mL) was heated at 200 °C under argon for 3 h. The reaction mixture was poured into water (800 mL), and the precipitate was collected and washed with methanol (500 mL × 2). This gave the cyano-terminated hyperbranched poly-(ether ketone), **7**, as a brown solid; 92%. IR: 2230, 1660, 1580, 1500, 1430, 1300, 1230 cm^{-1}.

Relaxation and Motion-Solid-State ^{1}H NMR Spectroscopy. Measurement of ^{1}H spin−lattice relaxation times in the rotating frame, $T_{1\rho}$, at the variable temperatures (140−400 K) for FHBPEK, FHBPEK-CMs, CHBPEK, and LPEK were performed with a Bruker model MSL-200 spectrometer (200.13 MHz for ^{1}H). A ^{1}H spin-lock-delay τ pulse sequence was employed with [1]H 90° pulse width of 4.5 μs and the repetition time of ca. 5 T_1 for the net magnetization to be completely relaxed. Typically 15−20 different τ values were used, and the free induction decay (FID) signals accumulated for the several hundred times were Fourier transformed and then integrated to obtain the decay curve. The various temperatures were established by regulating the heat current in steady dry-air flow over room temperature and in steady cold nitrogen gas flow from the dewar below room temperature.

Results and Discussion

Synthesis. The monomer 3,5-difluoro-4′-hydroxybenzophenone, **2**, used for the preparation of the fluoro-terminated hyperbranched poly(ether ketone) (FHBPEK) was synthesized according to the reaction developed by Hawker.[17] The core molecule **4** was synthesized by Friedel−Crafts acylation reaction in 71% yield to control and vary the degree of branching of FHBPEK. Polymerization of **2** with different mole ratio of **4** (mol % of 1.9 and 3.4, respectively) in the presence of K$_2$CO$_3$ in NMP at 150−200 °C for 6 h produced two FHBPEKs (FHBPEK-CM01 and -02, respectively), **5**, having different degrees of branching. Furthermore, to investigate and compare the role of the hyperbranched structure against the linear analogue, the linear poly(ether ketone) (LPEK), **6**, was prepared from 4,4′-difluorobenzophenone and resorcinol in the presence of K$_2$CO$_3$ in NMP at reflux for 3 h in 95% yield. The resorcinol used

Scheme 1
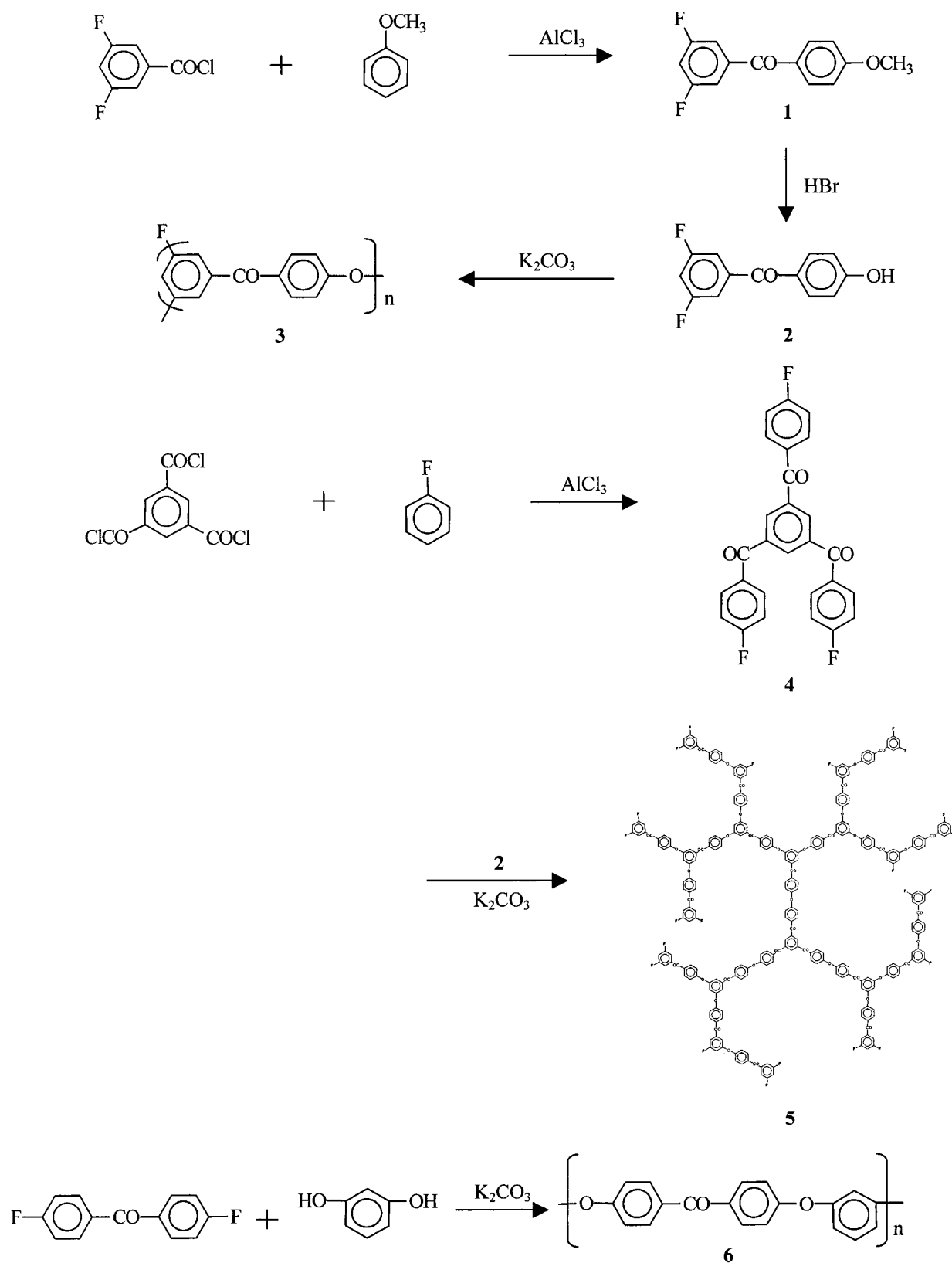
in the synthetic route of LPEK imparted an irregular, molecularly kinked structure, thereby providing an improved solubility in the common solvents and hence a convenience in sample preparation and characterization. In addition, the fluoro groups of FHBPEK were chemically substituted by the cyano groups via reaction of **3** with 4-cyanophenol (Scheme 2). The resulting cyano-terminated hyperbranched poly(ether ketone) (CHBPEK) was prepared for the purpose of comparison with FHBPEK. From the IR spectra of CHBPEK, the band appearing at 2230 cm^{-1} confirmed the substitution of fluoride with cyanide.

General Properties. a. Molecular Weight and Glass Transition Temperature (T_g). Molecular

Scheme 2
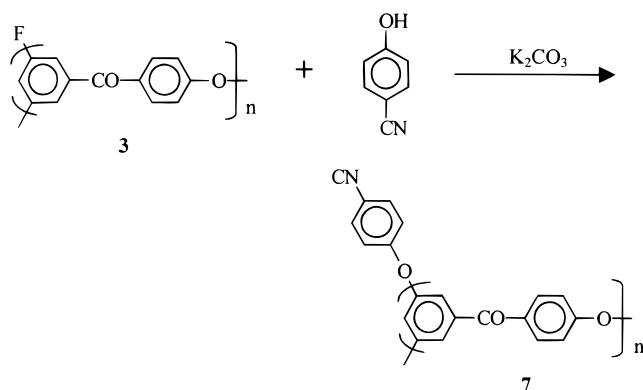
weights of the three different FHBPEKs and the LPEK were determined by GPC analysis calibrated with linear polystyrene standards. Hyperbranched polymers, in comparison with their linear analogues, are generally expected to exhibit the lower molecular weight.[18] This is mainly ascribed to the smaller hydrodynamic volume which results from the higher branching than is found in for its linear counterpart of the same molecular weight. Thus, the determination of the molecular weights of FHBPEKs by GPC in comparison to linear polystyrene standards is considered to be similar to or slightly higher than those of LPEK.[18] The results of the number-average molecular weights (M_n) and the polydispersity index for FHBPEKs and LPEK are shown in Table 1.

Differential scanning calorimetry (DSC) was used to characterize the thermal transitions. The glass transition temperatures, T_g's, of the FHBPEKs decreased as the degrees of branching increased. Shorter branches of FHBPEK-CM01 and -CM02 compared to that of FHBPEK probably cause the thermal transition to occur at the lower temperatures.

b. Degree of Branching (DB). The degree of branching (DB) is one of the most important molecular parameters of hyperbranched polymers since it determines the difference in molecular structure in comparison with linear polymers. For an ideal dendrimer, DB is equal to 1. A hyperbranched polymer will take DB values between 0 and 1. Fréchet et al. proposed a definition for the degree of branching of hyperbanched polymers formed in the polycondensation of AB₂-type monomers:[19]

$$\mathrm{DB}_{\mathrm{Frechet}} = \frac{D + T}{D + T + L} \qquad (1)$$

where, D, T, and L are the fraction of dendritically, terminally, and linearly incorporated monomers. Hölter et al. also proposed that in large hyperbranched molecules (i.e., at high conversions in the course of the reaction) T and D become practically identical in one molecule. Therefore, the following equation is employed:[20]

$$\mathrm{DB}_{\mathrm{Holter}} = \frac{2T}{2T + L} \qquad (2)$$

The ¹⁹F NMR spectrum of FHBPEK shows a major peak at −107.7 ppm (a) due to the fluorides of the terminal unit, while the peak at −108.5 ppm (b) is assigned to those of the linear unit (Figure 1). Integration of each peak allows the relative numbers of fluorides in the terminal and the linear unit. Thus,

calculation of DB for FHBPEK prepared in this study gives the value of 0.49, which is consistent with a statistically branched structure as proposed by Flory for an AB₂ system.[21] According to the statistical analyses of Radke et al., the degree of branching obtained in polycondensation of AB₂ monomers approaches DB = ²/₃ in the presence of core molecule, which is in good agreement with our experimental results.[22]

Local Relaxation and Molecular Motion. As our interest is focused on molecular motions, ¹H spin−lattice relaxation time in the rotating frame, $T_{1\rho}$, was directly measured as a function of temperature by using the appropriate pulse sequence, ¹H-spin-lock-τ-pulse. First, a $\pi/2$ rf pulse along x rotates M_0 into the xy plane (M_{xy}) along the y axis. Immediately following this pulse, B_1 is shifted in phase by 90° in the xy plane so that it lies along the y axis, collinear with M_{xy}. The magnetization along the y axis can be monitored as a function of delay time, τ, by turning B_1 off and activating the receiver at time τ.[23] Refer to the following equation:

$$M(\tau) = M_0 \exp(-\tau/T_{1\rho}) \qquad (3)$$

where M_0 is the intensity of the signal at $\tau \geq 5T_1$. $T_{1\rho}$ is the spin−lattice relaxation time in the rotating frame where the effective force is B_1. Such $T_{1\rho}$ relaxation time is analyzed in terms of appropriate model to obtain detailed information on molecular motions with low frequency (tens of kilohertz) particularly in the solid state. When the domains having different motions are present, the magnetization decay can be partitioned and expressed as the sum of exponential functions as number as the domains,

$$M(\tau) = \sum_i M_{0,i} \exp(-\tau/T_{1\rho,i}) \qquad (4)$$

where i is the number of phases in the polymer system.

Figure 2 shows plots of ¹H $T_{1\rho}$ magnetization intensity versus delay time for three FHBPEKs and LPEK at 320 K. The $T_{1\rho}$ data of FHBPEKs and LPEK were tried to be nonlinear least-squares fit to either eq 3 or eq 4, depending on the standard error of estimate (R^2) for each case. The magnetization of LPEK decayed with a single-exponential function being fit well to eq 3 (Figure 2b). However, in all cases of FHBPEKs, the $T_{1\rho}$ relaxation decay curves fitted into two exponentials having different $T_{1\rho}$'s by an order of magnitude with each other, indicating there existed two different motional phases, A and B (Figure 2a), given by the following equation:

$$M(\tau) = M_{0,\mathrm{A}} \exp(-\tau/T_{1\rho,\mathrm{A}}) + M_{0,\mathrm{B}} \exp(-\tau/T_{1\rho,\mathrm{B}}) \qquad (5)$$

Recognizing that two possible regions for the different motional phases in hyperbranched polymers are linear and terminal/branched regions, the assignment of the two components A and B of the FHBPEKs into the individual regions were performed by (i) determining the correlation time, τ_c, of A and B phases, (ii) analyzing the ¹⁹F NMR spectra of both FHBPEK and CHBPEK to see whether the end groups were substituted from fluorine to cyanide on both A and B phases, and finally (iii) comparing the τ_c's of both regions of FHBPEK with those of corresponding regions of CHBPEK to check the chance of the motional change induced by the end group substitution.

The temperature dependence of the resulting $T_{1\rho}$'s in the range 140−400 K for each portion of FHBPEKs and

Table 1. Characteristics of Hyperbranched Poly(ether ketone)s and Their Linear Counterpart

sample	molar proportion monomer/core molecule	M_n (g/mol)	polydispersity index	T_g (°C)	degree of branching
FHBPEK	100/0	14 500	15	145	0.49
FHBPEK-CM01	57/1	12 300	8	138	0.62
FHBPEK-CM02	28/1	11000	2.5	130	0.67
LPEK		15 400	1.4	123	
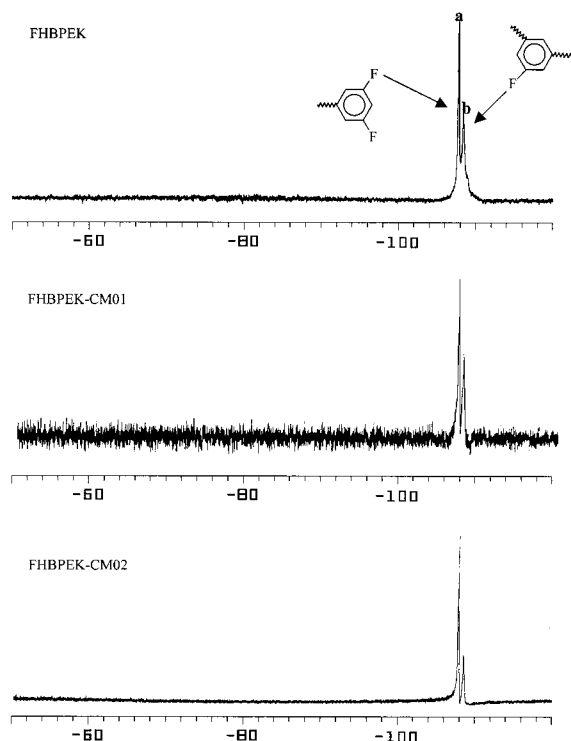
Figure 1. ^{19}F NMR spectra of FHBPEK, FHBPEK-CM01, and FHBPEK-CM02.

260−420 K for LPEK is shown in Figures 3 and 4, respectively. $T_{1\rho}$ plots versus reciprocal temperature exhibit a minimum, which indicates the most efficient relaxation; the $T_{1\rho}$'s located on the right side of the minimum imply the slow motion, and vice versa. It is noteworthy that even the same value of $T_{1\rho}$'s may be in very different motional states, depending on whether they are located on the slow side or the fast side of the minimum. Thus, to avoid such confusion and to relate $T_{1\rho}$'s to molecular mobility, it is necessary to determine the correlation time, τ_c, for which quantitative analyses by BPP/KT[15,16,24] theory provide relationships between the relaxation rate, internuclear distance, resonance frequency, and spectral density function of molecular motion (i.e., a measure of relative amount of motion). For protons, the principal mechanism of relaxation is through the time-dependent dipolar interaction, and the relaxation rates are given by

$$\frac{1}{T_{1\rho}} = \frac{3}{2}\gamma^4\hbar^2 I(I+1)\left[\frac{1}{4}J(2\omega_1) + \frac{5}{2}J(\omega_0) + \frac{1}{4}J(2\omega_0)\right] \quad (6)$$

where γ is the proton magnetogyric ratio, $\hbar$ is Planck's constant divided by 2π, r is the distance between coupled spins, I is the spin quantum number $(=\frac{1}{2})$, $J(\omega)$ is the spectral density function at particular frequency, ω_1 is spin-lock field frequency, and ω_0 is the Larmor

frequency. Since $J(\omega)$ is given by

$$J(2\omega_1) = \frac{24}{15r^6}\left[\frac{\tau_c}{1 + 4\omega_1^2\tau_c^2}\right] \quad (a)$$

$$J(\omega_0) = \frac{4}{15r^6}\left[\frac{\tau_c}{1 + \omega_0^2\tau_c^2}\right] \quad (b)$$

$$J(2\omega_0) = \frac{16}{15r^6}\left[\frac{\tau_c}{1 + 4\omega_0^2\tau_c^2}\right] \quad (c)$$

the relation between relaxation and molecular motion is established as

$$\frac{1}{T_{1\rho}} = \frac{3}{10r^6}\gamma^4\hbar^2\left[\frac{\frac{5}{2}\tau_c}{1 + \omega_0^2\tau_c^2} + \frac{\tau_c}{1 + 4\omega_0^2\tau_c^2} + \frac{\frac{3}{2}\tau_c}{1 + 4\omega_1^2\tau_c^2}\right] \quad (7)$$

With this relation, τ_c values can be extracted by nonlinear curve fitting of $T_{1\rho}$ data at the corresponding temperatures. The τ_c values versus inverse temperature for FHBPEKs in the temperature range 140−400 K are shown in Figures 5 and 6. The molecular mobility of the portion A of FHBPEKs enhanced as the degrees of branching increased (Figure 5). On the other hand, the molecular mobility of the B portion of FHBPEKs was little affected by the degree of branching, particularly at the temperatures below room temperature, but became gradually higher as the degree of branching increased at the temperatures greater than room temperature (Figure 6). From these results, the τ_c became shorter and hence the molecular mobility increased especially at the portion A as the degree of branching of FHBPEKs increased.

To assign each portion A and B, a model study was performed with cyano-terminated hyperbranched poly-(ether ketone) (CHBPEK) which fluorine groups of FHBPEK were substituted with cyanophenol by nucleophilic displacement (Scheme 2). The effect of cyano substitution on FHBPEK and the degree of substitution (DS) for CHBPEK were analyzed and determined by ^{19}F NMR spectroscopy. Figure 7 shows ^{19}F NMR spectra of FHBPEK and CHBPEK. In comparison of both spectra, the peak of CHBPEK must be the residual fluorine groups, which has not been substituted. Thus, the DS was calculated with the following equation, and the value was determined to be about 71%.

$$DS = \left(1 - \frac{\text{integral of CHBPEK}}{\text{integral of FHBPEK}}\right) \times 100 \quad (8)$$

As also seen in the spectra, the peak $(-107.7\ \text{ppm})$ for the terminal units of FHBPEK disappeared after the cyano substitutions whereas the signal $(-108.3\ \text{ppm})$ of the linear units still remained (Figure 7). The peak
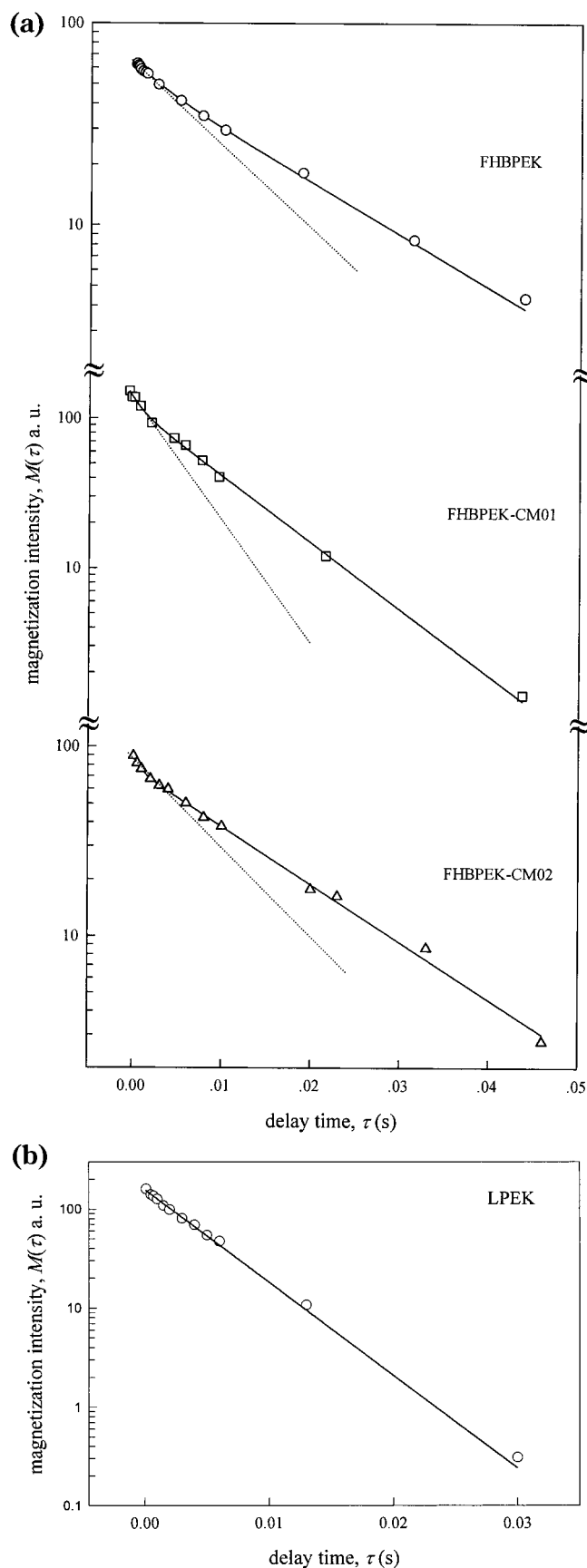
(a)

Figure 2. Magnetization intensity versus delay times at 320 K for (a) FHBPEK (○), FHBPEK-CM01 (□), and FHBPEK-CM02 (△) and (b) LPEK. The solid lines are the fits (a) to eq 5 for FHBPEKs and (b) to eq 3 for LPEK.

of CHBPEK became a little broader because it might include fluorines of both the linear and the monosub-
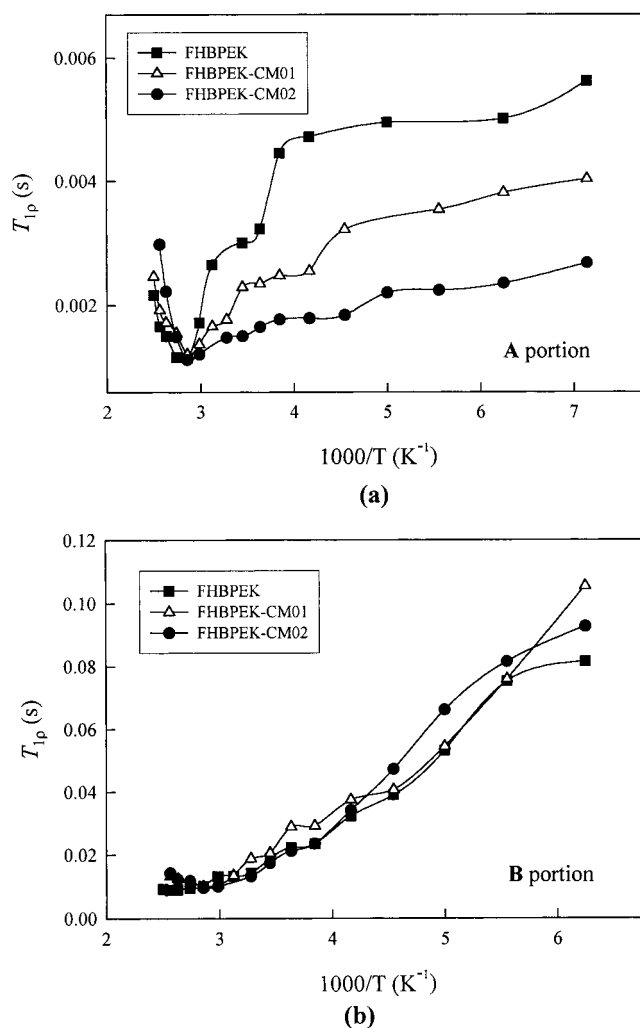

Figure 3. Temperature dependence of spin–lattice relaxation time in the rotating frame, $T_{1\rho}$'s, for FHBPEK (■), FHBPEK-CM01 (△), and FHBPEK-CM02 (●): (a) A portion and (b) B portion.
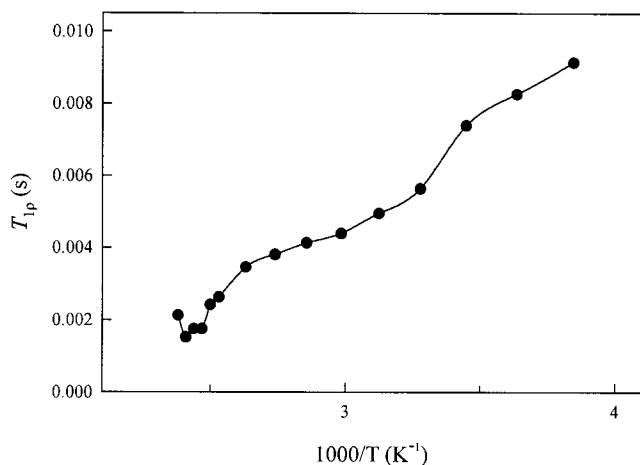
Figure 4. Temperature dependence of spin–lattice relaxation time in the rotating frame, $T_{1\rho}$, for LPEK.

stituted terminal units. The reactivity of the three possible substitution reactions, i.e., (i) monosubstitution, (ii) disubstitution of the terminal F groups, and (iii) substitution of the linear F groups, was determined by semiempirical molecular orbital calculations on the electronic charge and electron density at electrophilic centers of nucleophilic aromatic substitution using PM3
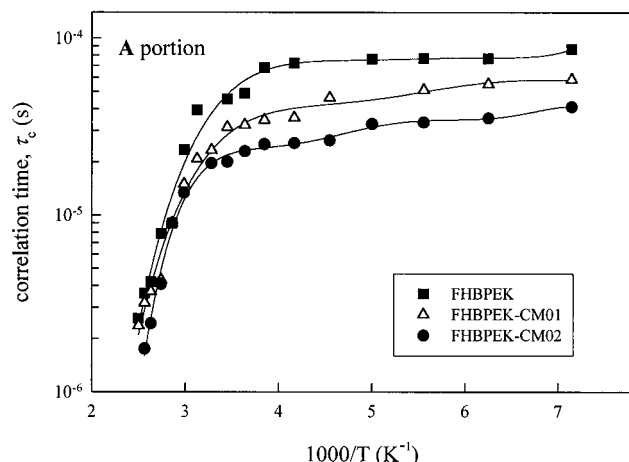
Figure 5. Correlation time, τ_c, versus inverse temperature for portion A of FHBPEK (■), FHBPEK-CM01 (△), and FHBPEK-CM02 (●) from 140 to 400 K.
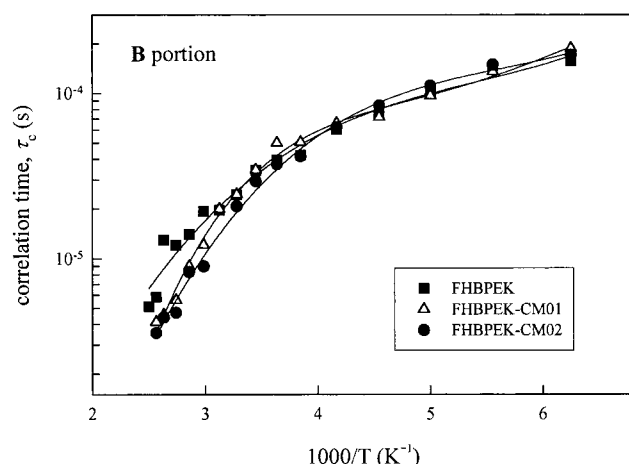

Figure 6. Correlation time, τ_c, versus inverse temperature for portion B of FHBPEK (■), FHBPEK-CM01 (△), and FHBPEK-CM02 (●) from 140 to 400 K.

formalism in HyperChem v.5.0. The reactivity was in the order of higher to lower (i), (ii), and (iii). Thus, the fluorine peaks of the CHBPEK were more dominated by the fluorines of the linear groups.

CHBPEK exhibited two-component (A and B phases) $T_{1\rho}$ relaxation decay behavior, although not shown here, similarly as for the FHBPEKs. In determination and comparison of τ_c's of CHBPEK with those of FHBPEK, two polymers had similar τ_c values at portion A, whereas CHBPEK had much shorter τ_c than FHBPEK at portion B (Figure 8). Recognizing that the dominant fluorines remaining in the signal of CHBPEK were those of the linear units, portion A must be assigned to the linear units and portion B to the terminal/branched.

To investigate the difference in the local molecular motion for the hyperbranched versus linear polymers and the effect of molecular structure on the mobility, the τ_c's of the linear portion of FHBPEKs were compared with those of the linear analogue LPEK in the temperature range 260−400 K (Figure 9). Despite the fact that FHBPEKs had a chemical unit structure and actual molecular weight similar to or somewhat higher than those of LPEK, the FHBPEKs had shorter correlation times and hence higher local molecular mobility compared to the LPEK, especially at the temperature above room temperature. This result meant that the hyperbranched structure imparted faster molecular motion
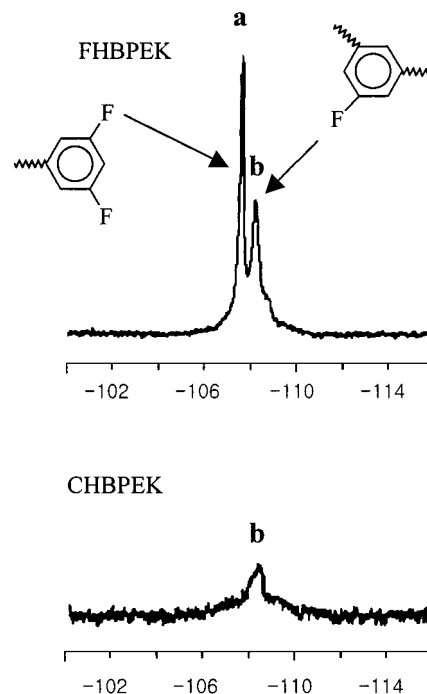

Figure 7. ^{19}F NMR spectra of FHBPEK and CHBPEK.

than the linear structure, and the difference became larger as the temperature increased.

Further insight into the molecular motion is to determine the activation energy, E_a, which corresponds to the barrier height for the potential hindering motion. It has been well-known that the temperature dependence of correlation time of linear polymer follows an Arrhenius expression as follows:[25]

$$\tau_c = \tau_{c,0} \exp(E_a/RT) \qquad (9)$$

where $\tau_{c,0}$ is the correlation time at infinite temperature and R is the molar gas constant. As seen in Figure 9, the τ_c of LPEK was solely a linear function of the temperature through an Arrhenius relation, and the activation energy was calculated to be about 10.12 kJ/mol. On the contrary, the FHBPEKs did not show the Arrhenius behavior. In such a case, the activation energies could be estimated from the $T_{1\rho}$ versus reciprocal temperature plots; at the lower temperature side (i.e., the right side of the minimum), $T_{1\rho}$ is directly proportional to τ_c and hence $T_{1\rho} \propto \exp(E_a/RT)$. Thus, the E_a value is obtained from the slope of the low-temperature side of the minimum ($\omega\tau_c \geq 1$) in the logarithmic plot of $T_{1\rho}$ against $1/T$. The activation energies of FHBPEKs were lower than that of LPEK and decreased in the sequence of FHBPEK, FHBPEK-CM01, and FHBPEK-CM02 (Table 2). The ordering in E_a's was in good agreement with the trend in τ_c's, indicating the higher molecular mobility as the hyperbranched structures were endowed and as the degrees of branching increased.

Conclusions

1. The degrees of branching were controlled by the amount of core molecules used, resulting in 0.49 for FHBPEK, 0.62 for FHBPEK-CM01, and 0.67 for FHBPEK-CM02.

2. From the solid-state ^{1}H NMR $T_{1\rho}$ relaxation studies, FHBPEKs showed the two-component exponential
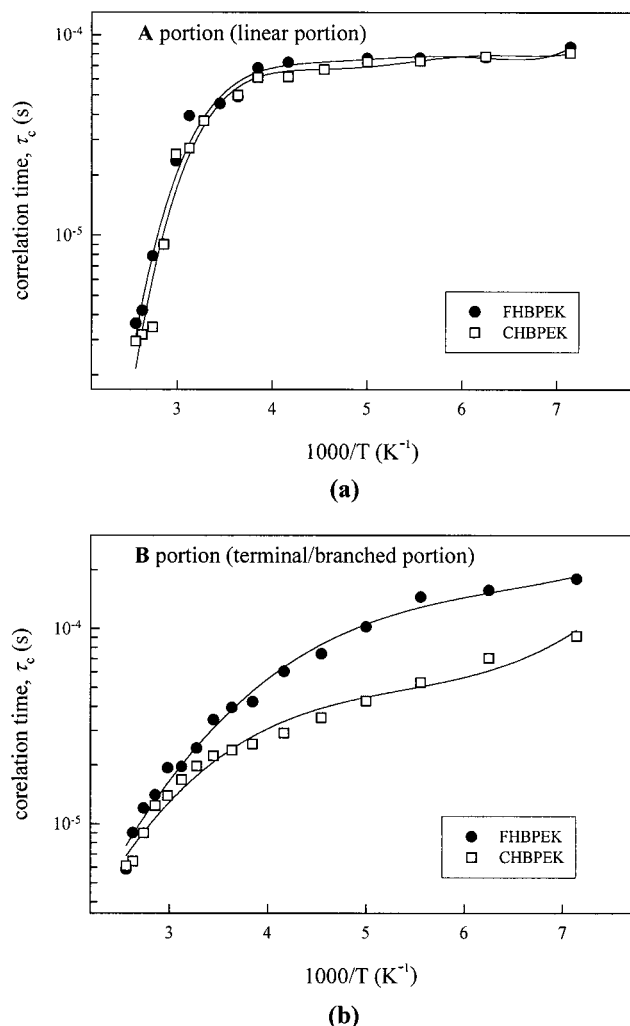
Figure 8. Correlation time, τ_c, versus inverse temperature for FHBPEK (●) and CHBPEK (□): (a) A portion (linear portion) and (b) B portion (terminal/branched portion).
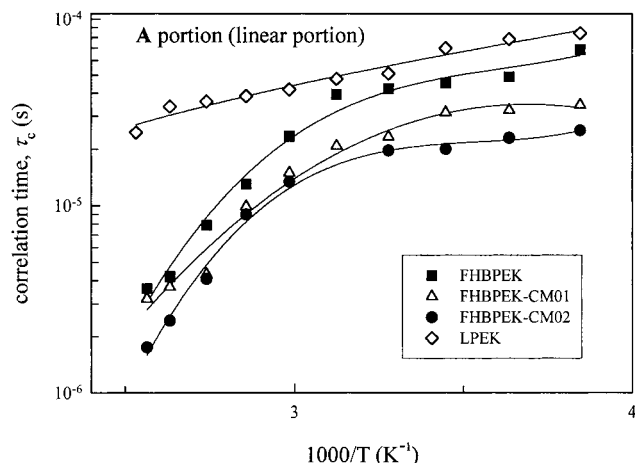

Figure 9. Correlation time, τ_c, versus inverse temperature for A portion (linear portion) of FHBPEK (■), FHBPEK-CM01 (△), FHBPEK-CM02 (●), and LPEK (◇) from 260 to 400 K.

decay with the time constants $T_{1\rho,A}$ and $T_{1\rho,B}$, indicating the presence of two portions (A and B) of different motion.

3. From the comparison of the correlation times, τ_c's, and ^{19}F NMR spectra of FHBPEK with those of end-group-substituted hyperbranched poly(ether ketone),

Table 2. Activation Energy of Hyperbranched Poly(ether ketone)s and Their Linear Counterpart

	E_a (kJ/mol)	
sample	linear portion	terminal/branched portion
FHBPEK	8.50	6.16
FHBPEK-CM01	3.23	5.60
FHBPEK-CM02	1.82	4.88
LPEK	10.12	

CHBPEK, each portion was assigned as linear or terminal/branched, respectively.

4. From the measurement of the correlation time, τ_c, and the activation energy, E_a, it was concluded that the molecular motion of the linear portion of FHBPEKs was faster than that of LPEK and enhanced with increase degree of branching through the entire range of experimental temperatures. On the other hand, the molecular mobility of the terminal/branched portion of FHBPEKs was little affected by degrees of branching at the temperatures below room temperature but showed the same trend as the linear portion above room temperature.

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