

Dynamical heterogeneity and molecular mobility of hyperbranched poly(ether ketone)s with respect to the homologous linear

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Abstract

Hyperbranched poly(ether ketone) (HBPEK) with fluoro-end groups (F-HBPEK) was synthesized by a one-step polymerization reaction. Another HBPEK with different end groups, i.e. cyano-terminated HBPEK (C-HBPEK), was prepared by chemical modification of the fluorides in FHBPEK with cyanophenols. Through analysis by ^{19}F nuclear magnetic resonance (NMR) spectroscopy, the degree of modification from fluorine to cyano groups was determined to be 71%. Furthermore, it was confirmed that the most of the cyano groups were substituted on to the terminal units rather than the linear units. Dynamical heterogeneity/homogeneity and corresponding molecular mobility of both F- and C-HBPEK were investigated by a solid-state ^1H NMR spectroscopy. The results were then compared to those of linear analogous poly(ether ketone) (LPEK), which was prepared to investigate any difference in these two characteristics due to their structural dissimilarity. Analysis of ^1H magnetization decay as a function of delay time determined the spin–lattice relaxation time in the rotating frame, $T_{1\rho}$. The double-exponential decay of $T_{1\rho}$ relaxation of both F- and C-HBPEK indicated coexistence of dynamically heterogeneous phases on the basis of motional difference; each was assigned to be the linear and the branched/terminal phase, respectively. In contrast, the single decay in LPEK confirmed a dynamical homogeneity. From further measurements of $T_{1\rho}$ s over the temperature range of 140–400 K, the correlation times, τ_c s, and the activation energies, E_a s, were determined. The dynamics of the branched/terminal phase of HBPEKs was greatly affected by the nature of end-group modification. The molecular motion of the linear phase of HBPEKs was faster than that of LPEK, indicating that the hyperbranched structure was responsible for the higher molecular mobility than the linear structure. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Hyperbranched poly(ether ketone); Solid-state pulsed wide-line ^1H NMR spectroscopy; Relaxation behavior

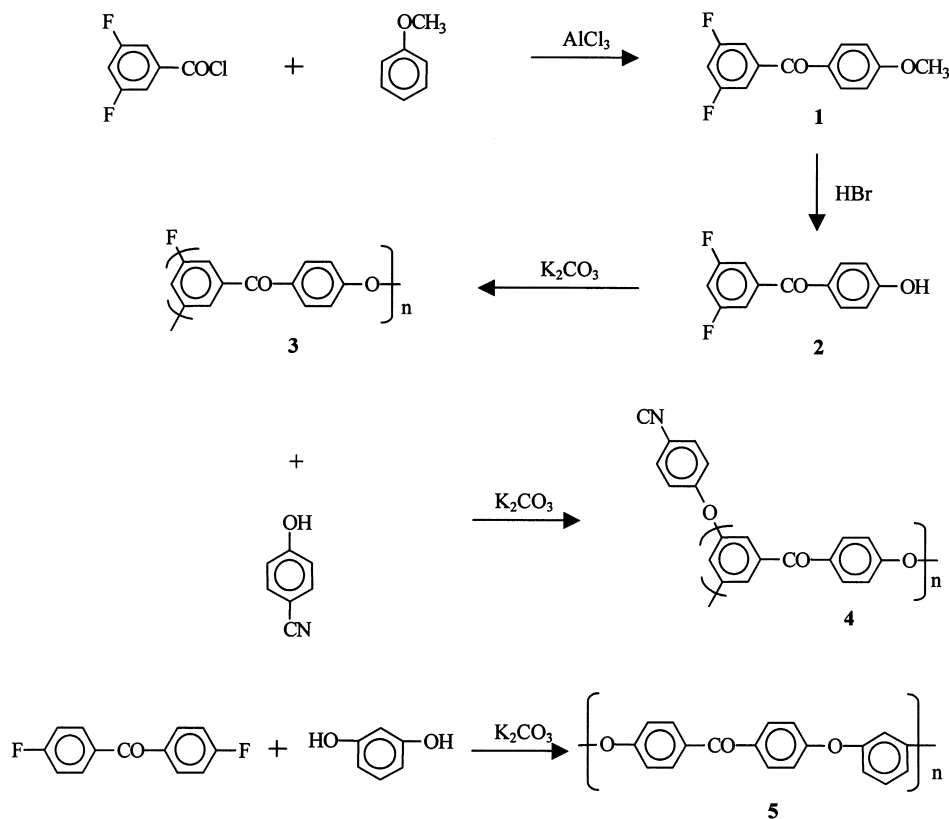
1. Introduction

Hyperbranched polymers (HBPs) are a unique class of dendritic polymers (dendrimers and hyperbranched polymers) that are characterized by a highly branched three-dimensional structure and a large number of chain ends [1–3]. Although the dendrimers and the hyperbranched polymers are based on AB_x -type monomers, the former are monodisperse while the latter are dissimilar in the sense that they are poly-disperse and contain linear segments [4–6]. However, several of the unusual properties of dendritic polymers, such as low viscosity, high solubility, and lack of significant entanglement, are also exhibited in HBPs [7,8]. The one-step polymerization processes are advantageous as they allow HBPs to be more readily available at low costs and to be produced on a large scale for the practically potential

applications [9,10]. Therefore, HBPs possessing very unique properties and produced by simple synthetic routes are better-suited for applications that exploit the final physical/mechanical properties [11,12].

The dynamical heterogeneity or homogeneity of polymers in the solid state is interdependent with structure and the corresponding local motion is strongly related to the physical/mechanical properties in their end use. Nevertheless, studies to characterize and understand the dynamic heterogeneity/homogeneity–molecular motion relationships, in conjunction with the structural dissimilarity have not been extensively accomplished. A very convenient and powerful means that can reveal any discrimination of motional heterogeneous regions (i.e. branched/terminal and linear units) within an HBP and the details of the corresponding molecular motion is solid-state nuclear magnetic resonance (NMR) spectroscopy with pulsed wide-line for ^1H [13–16]. This can provide a convenient way to obtain information about average local motion in a whole

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Scheme 1.

polymeric system. For the polymers in the solid state, the usually measured parameter is ^1H spin–lattice relaxation time in the rotating frame, $T_{1\rho}$. The dynamical heterogeneity or homogeneity can be identified by the decay behavior of ^1H magnetization for $T_{1\rho}$ relaxation. Furthermore, from the variable temperature measurements of $T_{1\rho}$ s, the correlation time, τ_c , is determined on the basis of Bloembergen–Purcell–Pound (BPP) and Kubo–Tomita (KT) theory [17–20]. The correlation time, τ_c , is defined as the average time required for motional events and commonly expresses the molecular mobility of polymers. BPP/KT theory represents a decrease in τ_c as the motion gets faster and hence the mobility increases.

In this present paper, we focus on the dynamical heterogeneity of hyperbranched poly(ether ketone)s, (F- and C-HBPEK), in comparison to their linear analogous poly(ether ketone) (LPEK) and the corresponding local mobility of each phase with respect to the nature of the end groups as well as the difference of hyperbranched versus linear structures. For this purpose, we employed a solid-state pulsed wide-line ^1H NMR spectroscopy and selected appropriate experimental NMR protocol, spin–lattice relaxation time in the rotating frame, $T_{1\rho}$, with variable temperatures, which can give information on molecular motions with low frequency (tens of kilohertz) particularly in the solid state.

2. Experimental section

2.1. Materials

3,5-difluoro-4'-hydroxybenzophenone, **2**, used for the preparation of the corresponding hyperbranched poly(ether ketone) (F-HBPEK), **3**, was synthesized as described by Hawker (Scheme 1). The structural verification of **2** and **3** has been described elsewhere [21]. Cyano-terminated hyperbranched poly(ether ketone) (C-HBPEK), **4**, was synthesized by the reaction of **3** with 4-cyanophenol, in which the fluorine groups of F-HBPEK were substituted with the cyanide groups by nucleophilic displacement. The substitution of the cyano group was confirmed by the appearance of a strong peak in the IR at 2230 cm^{-1} corresponding to the CN stretching. Linear poly(ether ketone) (LPEK), **5**, which had similar chemical unit structure and molecular weight to **3** and **4**, was synthesized from 4,4'-difluorobenzophenone and resorcinol in the presence of K_2CO_3 in NMP at reflux for 3 h in 95% yield. It is noteworthy that the resorcinol used in the synthetic route of LPEK imparted an irregular and molecularly kinked structure, thereby providing an improved solubility in a common solvent and hence a convenience in sample preparation and characterization.

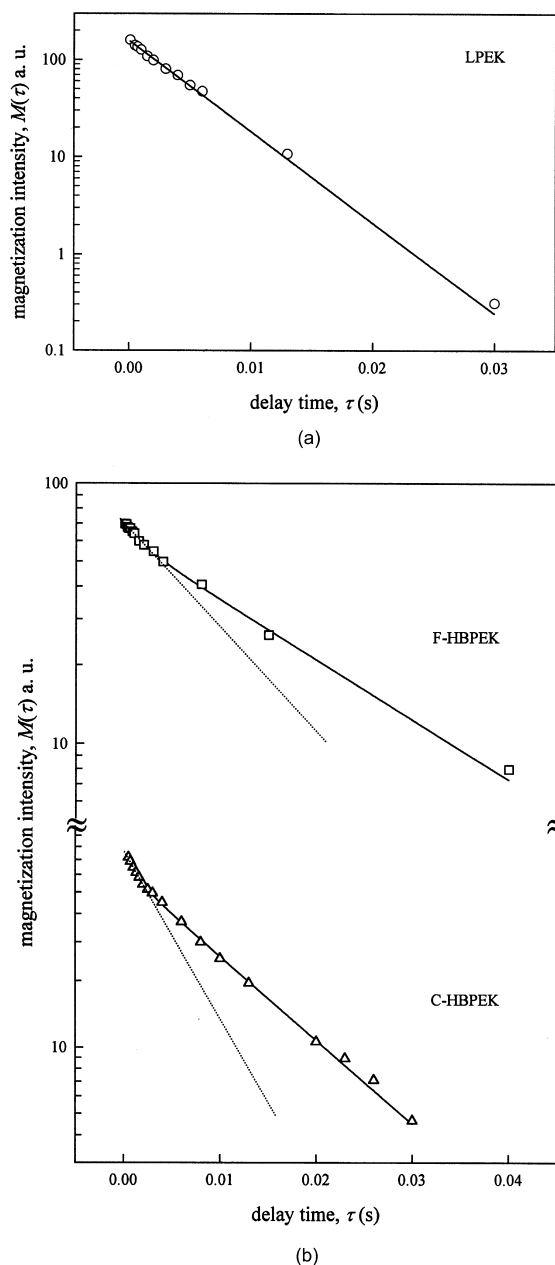


Fig. 1. Logarithmic plot of magnetization intensity versus delay time: (a) at 320 K for LPEK, and (b) at 290 K for HBPEKs. The solid lines are the fit (a) to Eq. (1) for LPEK, and (b) to Eq. (2) for HBPEKs.

2.2. General directions

In order to analyze the degree of branching of the hyper-branched poly(ether ketone)s, ^{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 standard. Glass transition temperatures (T_g s) were measured on a Perkin–Elmer DSC 7 differential scanning calorimeter. The temperature was varied from 50 to 250°C at a heating rate of 20°C/min. Calculations of T_g were done by taking the midpoint of the inflection tangent, upon the second heating

scan. Gel permeation chromatography (GPC) was carried out on a Waters 600 with 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 the solvent. The M_n and M_w/M_n values were calculated from the GPC results based upon calibration with polystyrene standard.

2.3. Solid-state pulsed wide-line ^1H NMR spectroscopy

Measurements of ^1H spin–lattice relaxation times in the rotating frame, $T_{1\rho}$, at the variable temperatures (140–400 K) for F-HBPEK, C-HBPEK, and LPEK were performed with a Bruker model MSL-200 spectrometer (200.13 MHz for ^1H). A ^1H 90° pulse width of 4.5 μs was employed with free induction decay (FID) signal accumulations. The various temperatures were established, within an accuracy of ± 0.5 K, by regulating the heat-current in steady dry-air flow over the room temperature and in steady cold nitrogen gas flow from the liquid nitrogen dewar below the room temperature. $T_{1\rho}$ relaxation times were determined in the temperature range of 140–400 K with a ^1H spin-lock–delay τ pulse sequence.

3. Results and discussion

3.1. Analysis of dynamical heterogeneity/homogeneity

The plot of ^1H magnetization intensity versus delay time accomplishes the analysis of the relaxation behavior. The ^1H magnetization intensity decays exponentially with a time constant equal to $T_{1\rho}$, as follows [13]:

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

where, M_0 is the intensity of the signal at $\tau \geq 5T_1$ and $T_{1\rho}$, which is determined by a nonlinear least-squares fit using experimental data, is the spin–lattice relaxation time in the rotating frame based on the intramolecular dipole–dipole interactions arising from the molecular motion in the frequency range of tens of kilohertz under the ^1H spin-locking field. In Fig. 1, the logarithmic magnetization intensity is plotted against the delay time. As shown in Fig. 1a, the magnetization of LPEK at 320 K decays with a single-exponential function, being fit well to Eq. (1). Fitting of data at any other temperature, although not shown here, also represents a single-exponential, similarly to that of 320 K. These results indicate that LPEK is dynamically homogeneous with identical relaxation behavior. In contrast, since decay curves of F- and C-HBPEK do not appear to be single-exponential, they are analyzed in terms of a few components with different $T_{1\rho}$ s. F- and C-HBPEK show double-exponential decomposition in the $T_{1\rho}$ relaxation contributed from the two components, $T_{1\rho,A}$ and $T_{1\rho,B}$:

$$M(\tau) = M_{0,A} \exp(-\tau/T_{1\rho,A}) + M_{0,B} \exp(-\tau/T_{1\rho,B}) \quad (2)$$

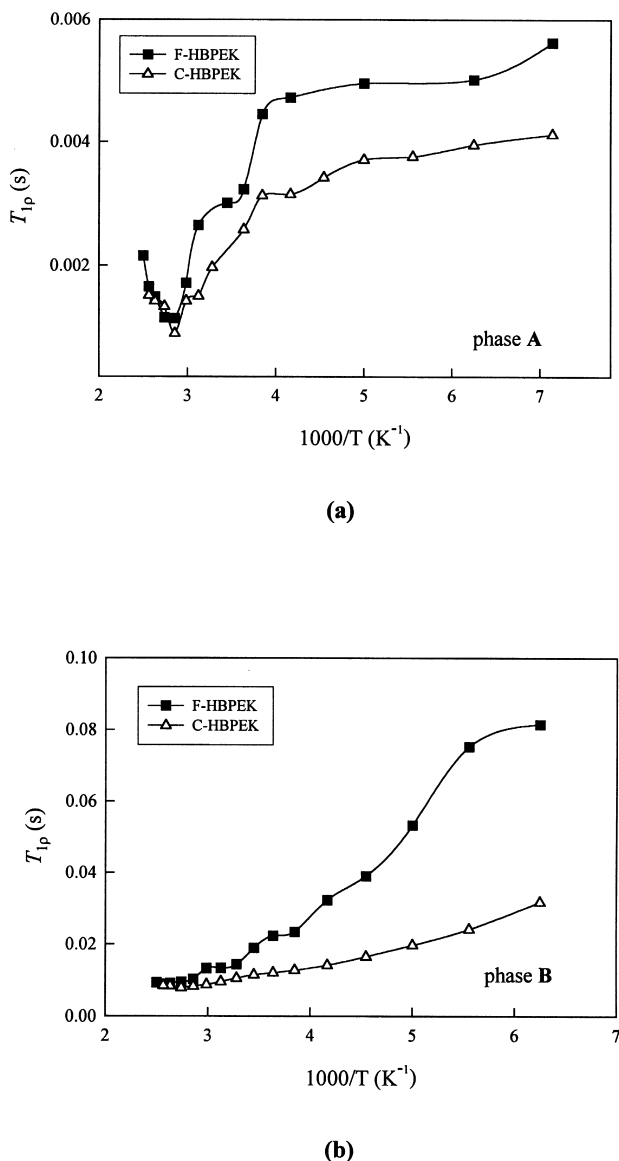


Fig. 2. ^1H spin-lattice relaxation time in the rotating frame, $T_{1\rho}$, versus inverse temperature for F-HBPEK (■) and C-HBPEK (△): (a) A phase, and (b) B phase.

Thus, they have the dissimilar motional phases, A and B, and are dynamically heterogeneous (Fig. 1b). It must be noted that two possible regions for the different motional phases in the hyperbranched polymers are the linear and the branched/terminal units, respectively. For the assignment of the two phases A and B of F- and C-HBPEK into the individual regions, various characterizations must be considered: (i) determination of correlation time, τ_c , of A and B phases, (ii) analysis of the ^{19}F NMR spectra of both F- and C-HBPEK to see whether the end groups from F to CN groups were substituted both on A and B phases or not, and finally (iii) comparison of the τ_c s of both regions of F-HBPEK with those of corresponding regions of C-HBPEK to check for any motional change induced by the end group modification.

3.2. Assignment of individual motional phases, A and B

The $T_{1\rho}$ variation as a function of inverse temperature in the range of 140–400 K is shown in Fig. 2 for individual phases (A and B) of HBPEKs. As the temperature increases, the $T_{1\rho}$ plot shows a minimum, which indicates the most efficient relaxation. It is noteworthy that even identical values of $T_{1\rho}$ s may be in different motional state, depending on whether they are located on the right side or the left side of the minimum. Thus, in order to relate $T_{1\rho}$ to molecular mobility, it is necessary to determine τ_c , which is a correlation time associated with the local molecular motion of less than two to three carbons.

The temperature dependence of $T_{1\rho}$ is characteristic of a single-activated process with correlation time, τ_c , for which quantitative analyses by BPP/KT theory provide relationship between the relaxation rate, internuclear distance, resonance frequency, and spectral density function of molecular motion (i.e. a measure of relative amount of motion) [17–20]. For protons, the principal mechanism of relaxation is through the time-dependent dipolar interaction, and the relaxation rates are given by

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

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 ($= 1/2$), $J(\omega)$ is the spectral density function at particular frequency, ω_1 is spin-lock field frequency, and ω_0 is Larmor frequency. Since $J(\omega)$ is given by

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

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

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

the relation between relaxation and molecular motion is established as

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

From Eq. (4), the correlation time, τ_c , for the individual protons were extracted by nonlinear curve fitting of $T_{1\rho}$ data at corresponding temperatures.

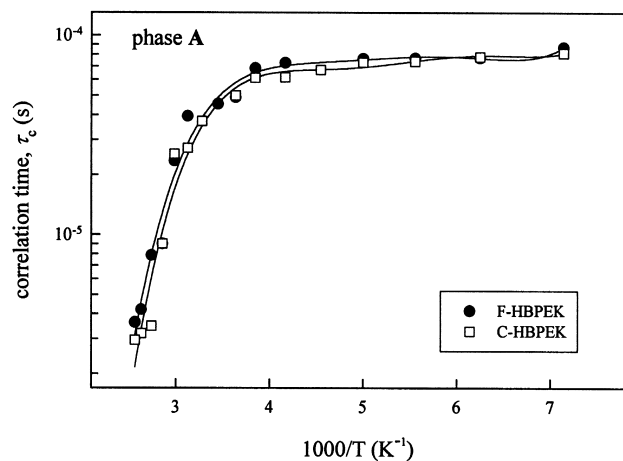


Fig. 3. Correlation time, τ_c , versus inverse temperature for the A phase of F-HBPEK (●) and C-HBPEK (□) from 140 to 400 K.

Figs. 3 and 4 showed the resulting τ_c s of F- and C-HBPEK for the two phases as a function of inverse temperature, respectively. For phase A, overall molecular mobility was little affected by the end-group change from F to CN groups. On the other hand, for phase B, the change of mobility by the end-group modification was very obvious. From these results, it was confirmed that the end group modification that generated the change of τ_c s was limited to the phase B.

Fig. 5 showed the ^{19}F NMR spectra of F- and C-HBPEK. Recognizing that the F-HBPEK involves individual terminal units with two fluorine groups and linear units with one fluorine group, the chemical environments and hence the chemical shifts of the terminal and linear units are different. ^{19}F NMR spectrum of F-HBPEK shows two characteristic resonances at -107.7 ppm (a) which correspond to the fluorides of the terminal unit and at -108.3 ppm (b) for the fluorides of the linear unit. As seen in Fig. 5, however, the signal of the terminal unit (-107.7 ppm) in the spectrum of C-HBPEK disappeared whereas that of the linear unit (-108.3 ppm) decreased a little, reflecting that most of the cyano-groups were substituted on to the terminal units rather than the linear units. Therefore, recognizing that the reactivity of the substitution of the cyano group was better at the terminal units rather than at the linear units (Fig. 5), phase A was assigned to be the linear phase and phase B the branched/terminal phase.

3.3. Analysis of local molecular mobility

Effect of end group modification. Prior to the analysis of

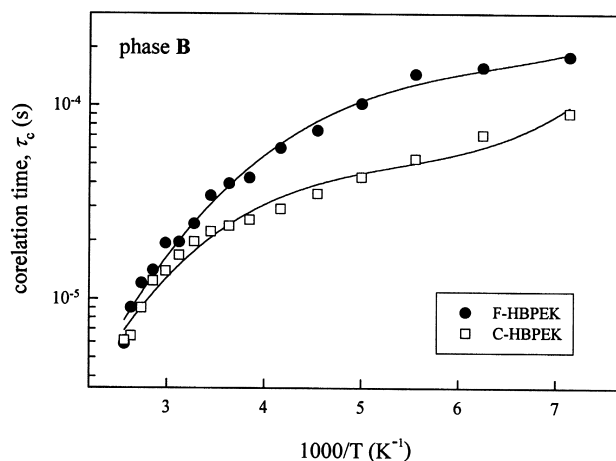


Fig. 4. Correlation time, τ_c , versus inverse temperature for the B phase of F-HBPEK (●) and C-HBPEK (□) from 140 to 400 K.

the effect of the end groups on the local molecular mobility, the degree of substitution of CN groups, the glass transition temperature, and the molecular weights of F- and C-HBPEK was determined. In Fig. 5, by taking the ratio of total integration of the C-HBPEK spectrum to that of the F-HBPEK spectrum, the degree of substitution of C-HBPEK could be calculated.

$$\text{Degree of substitution} = \left(1 - \frac{I(\text{C-HBPEK})}{I(\text{F-HBPEK})} \right) \quad (5)$$

where I is the total integration of the spectrum, i.e. $I(\text{F-HBPEK})$ is 67.33 and $I(\text{C-HBPEK})$ is 19.15. Thus, the degree of substitution was determined to be 0.71 or 71%. The glass transition temperature increased by 46°C , from 145 to 191°C , as one proceeded from a fluoro-terminated to an analogous cyano-terminated hyperbranched poly(ether ketone). This dramatic increase may be a result of the increase in the polarity of the chain ends (Table 1). C-HBPEK, end group modified of F-HBPEK, gave a GPC M_n of 9200 when that of the starting polymer, F-HBPEK, was 14 500. This is because of the fluorocarbon effect proposed by Mueller et al., in which the fluorocarbon content reduces the retention volume because of the nature of the lower frictional coefficient of the fluorides and hence increases the molecular weight by ca. 2 or 3 in the case of polyfluorinated materials [22]. Thus, on considering the fluorocarbon effect, the actual molecular weight of C-HBPEK was considered to be similar to or even more than that of F-HBPEK.

Figs. 3 and 4 showed the temperature variation of the

Table 1
General characteristics of F-HBPEK, C-HBPEK, and LPEK

Sample	Degree of substitution (%)	T_g ($^\circ\text{C}$)	M_n	MWD	Degree of branching
F-HBPEK		145	14500	15	0.49
C-HBPEK	71	191	9200	1.24	0.49
LPEK		123	15400	1.4	

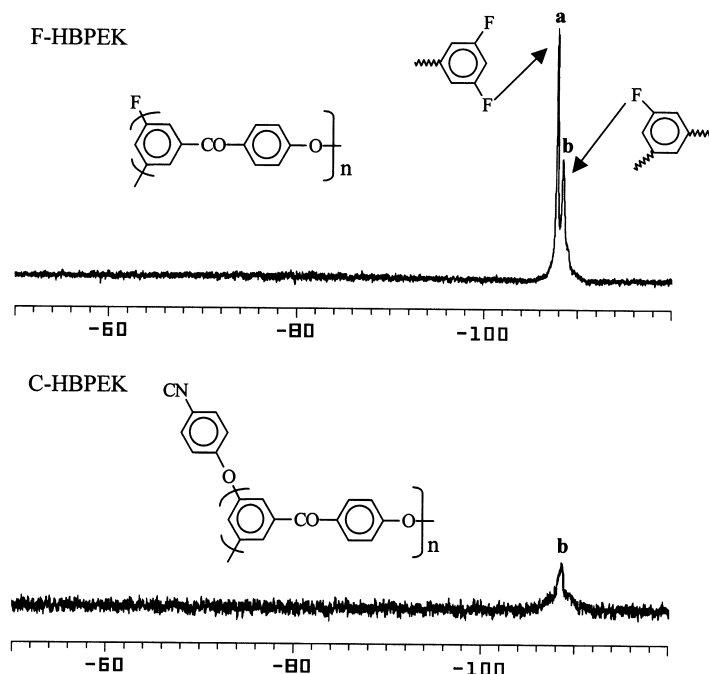


Fig. 5. ^{19}F NMR spectra of F-HBPEK and C-HBPEK.

correlation times obtained from $T_{1\rho}$ measurements. For the linear phase, τ_{cs} of F- and C-HBPEK decreased slightly at temperatures below the room temperature and dropped abruptly after the room temperature. In addition, the local molecular mobility was little affected by the nature of end groups because most of the end groups were substituted on to the terminal units rather than linear units. For the branched/terminal phase, the tendency of abrupt decrease of τ_{cs} was not clear, but the local molecular mobility was greatly affected by the nature of end groups. The glass transition temperature of C-HBPEK was higher than that of F-HBPEK, but the local motion determined by solid-state NMR spectroscopy was rather fast compared to that of F-HBPEK. This discrepancy might be ascribed to the fact that the glass transition temperature was related to the cooperative motions of 30–100 backbone carbons whereas correlation times were associated with the local motion of less than two to three carbons [23].

Effect of molecular architecture. To investigate the effect of the molecular architecture (i.e. hyperbranched versus linear) on the local molecular mobility, determination of the degrees of branching of HBPEKs and their molecular weights and LPEK were preceded and then, the τ_{cs} of the linear portion of hyperbranched polymers (F-HBPEK and C-HBPEK) were compared to those of LPEK.

A molecular parameter indicating the dissimilarity in molecular architecture between hyperbranched and linear polymers is the degree of branching (DB). The DB is commonly determined by NMR spectroscopy on the basis of low molecular weight model compounds,

which possess structures similar to the linear, dendritic, and terminal units in the respective HBPs. As first shown by Fréchet et al., the DB of a hyperbranched polymer is commonly calculated according to the following equation [24,25]:

$$\text{DB} = \frac{D + T}{D + T + L} \quad (6)$$

where, D , T , and L are the fraction of dendritically, terminally, and linearly incorporated monomers in the resulting hyperbranched polymers obtained from the respective signals in NMR spectra. Unlike dendrimers that are perfectly branched and have a DB of 1, hyperbranched polymers accept a certain degree of imperfection, i.e. the value of 0.4–0.8. However, for the degrees of branching of large hyperbranched polymers, where $D, T \gg L$, the following relationship was introduced by Hölter et al. [26].

$$\text{DB} = \frac{2D}{2D + L} \approx \frac{D + T}{D + T + L} \approx \frac{2T}{2T + L} \quad (7)$$

Integration of these well-resolved resonances in Fig. 5 allows the relative percentage of the terminal and linear units to be determined. From these values and Eq. (7), the degree of branching of F-HBPEK is calculated to be 0.49 or 49% and that of C-HBPEK was considered to be same. The molecular weights of HBPEKs and LPEK are determined by GPC analysis calibrated with polystyrene standards (Table 1). Hyperbranched polymers, in comparison to their linear analogues, are generally

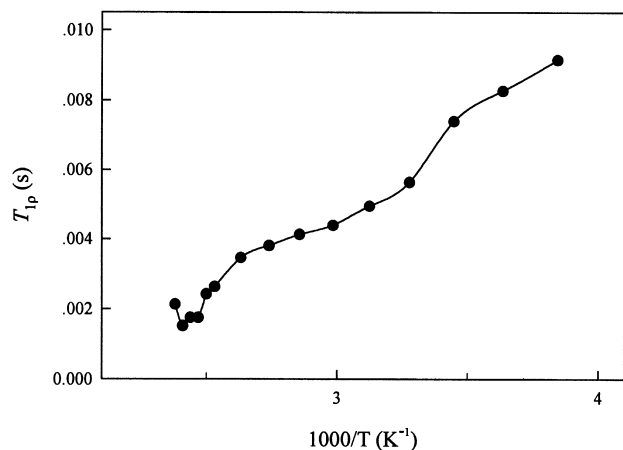


Fig. 6. ^1H spin–lattice relaxation time in the rotating frame, $T_{1\rho}$, versus inverse temperature for LPEK.

expected to exhibit lower molecular weights. This is mainly ascribed to the smaller hydrodynamic volume decreased by the high branching than for its linear counterpart of the same molar weight. Thus, the molecular weights of HBPEKs are considered to be similar to or even more than that of LPEK [12].

Fig. 6 showed the temperature dependence of $T_{1\rho}$ s in the temperature range of 260–420 K for LPEK. After applying the same procedure to HBPEKs, the corresponding correlation times were determined. Despite the fact that HBPEKs and LPEK had similar chemical unit structure and molecular weight, HBPEKs having degrees of branching of 0.49 had shorter correlation times and hence higher local molecular mobility than LPEK through the corresponding temperature range (Fig. 7). These results indicated that the hyperstructure imparted faster molecular motion than the linear structure through the entire range of experimental temperature, and the difference became larger as the temperature increased.

Activation energy. Further insight into the molecular motion helps to determine the activation energy, E_a [27]. For thermally activated motion, τ_c as a function of temperature is given by a simple Arrhenius expression, as follows:

$$\tau_c = \tau_{c,0} \exp(E_a/RT) \quad (8)$$

where, $\tau_{c,0}$ is the correlation time at infinite temperature and R is the molar gas constant. The activation energy is the barrier that must be overcome for reorientation to occur. For LPEK, the plot of the logarithm of the correlation time as a function of the inverse temperature was linear with a slope that was proportional to the activation energy (Fig. 7). From Fig. 7 and Eq. (8), the activation energy was calculated to be about 10.12 kJ/mol. In contrast, as seen in Figs. 5 and 6, the hyperbranched polymers did not follow the Arrhenius behavior. Thus, the activation energies were estimated from the slope of the lower temperature side of the minimum in the logarithmic plot of $T_{1\rho}$ versus $1/T$. The

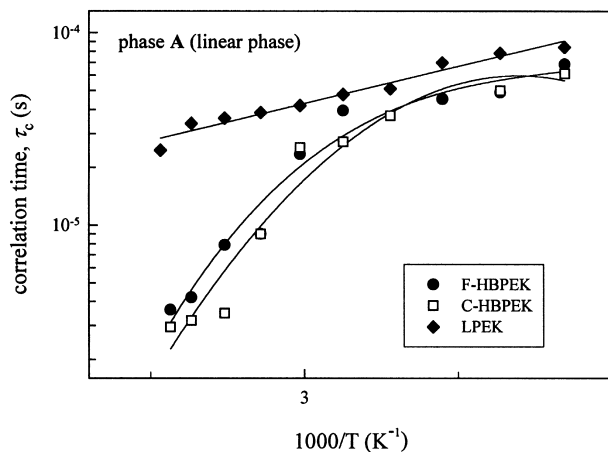


Fig. 7. Correlation time, τ_c , versus inverse temperature for linear phase of F-HBPEK (●), C-HBPEK (□), and LPEK (◆) from 260 to 400 K.

activation energies of HBPEKs showed the same trend as that of correlation times, but the difference between F-HBPEK and C-HBPEK in the linear phase was more prominent than the results of correlation time (Table 2).

4. Conclusions

This present paper gave details of dynamical/motional properties of hyperbranched poly(ether ketone)s in comparison to their linear counterpart.

1. From the measurements of spin–lattice relaxation time in the rotating frame, $T_{1\rho}$, by the solid-state pulsed wide-line ^1H NMR spectroscopy, hyperbranched poly(ether ketone)s were confirmed to be dynamically heterogeneous systems having two different motional phases, A and B, whereas LPEK demonstrated the single experimental relaxation behavior indicating that it was dynamically homogeneous.
2. To assign phases A and B, HBPEKs having two different end groups were prepared. C-HBPEK was end group modified from F-HBPEK and had a degree of substitution of 71%. From the results of correlation times and ^{19}F NMR spectra, each phase was assigned as linear and branched/terminal, respectively.
3. The correlation times exhibited that the local molecular mobility of HBPEKs was increased abruptly near the room temperatures whereas those of LPEK were enhanced

Table 2
Activation energies of F-HBPEK, C-HBPEK, and LPEK

Sample	E_a (kJ/mol)	
	Linear phase	Branched/terminal phase
F-HBPEK	8.50	6.16
C-HBPEK	5.98	3.07
LPEK	10.12	

linearly. Thus, it was confirmed that HBPEKs and LPEK showed different motional behavior because of the structural dissimilarity. In contrast, the branched/terminal phase of HBPEKs was greatly affected by the nature of end group functionality and presented that the local molecular mobility of C-HBPEK was rather enhanced as compared to F-HBPEK. The linear phase of HBPEKs whose degrees of branching were 0.49 had shorter correlation times and hence higher molecular mobility than LPEK through the corresponding temperature range.

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