Processability of Hyperbranched Poly(ether ketone)s with Different Degrees of Branching from Viewpoints of Molecular Mobility and Comparison with Their Linear Analogue

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ABSTRACT: Fluoro-terminated hyperbranched poly(ether ketone)s (FHBPEKs) with controlled degrees of branching and their linear analogous poly(ether ketone) (LPEK) whose chemical structure and molecular weights were similar to those of FHBPEKs were synthesized and characterized. Depending on the amount of the core molecules, degrees of branching of 0.49 (FHBPEK), 0.62 (FHBPEK−CM01), and 0.67 (FHBPEK−CM02) could be obtained with little variation in the number-average molecular weights of the three FHBPEKs. From the dynamic mechanical analyses, it was investigated that the crossover of the storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$ started to disappear at a critical value (> 0.62−0.67) of the degree of branching, indicating a nearly Newtonian or little entanglement flow. The correlation time, τ_c, was determined from the shear relaxation moduli and the Cole−Davidson equation, which provided a unique means to evaluate the melt processability on the basis of the molecular mobility. Highly branched structure of FHBPEKs predominantly increased the molecular mobility and enhanced the melt processability, realizing the optimum processing temperature lowered by 52−72 °C depending on the degree of branching, compared to that of LPEK. Further insights into the correlation times with the Vogel−Tamman−Fulcher (VTF) equation and the Arrhenius equation provided some novel information about the temperature dependence of the molecular mobility and the activation energy, in conjunction with the processability and the fragility of the FHBPEKs in comparison to the LPEK.

Introduction

Hyperbranched polymers (HBPs), prepared by one-pot processes wherein the AB_2-type monomers polymerize randomly and the resulting polymer can be produced in a large quantity at a reasonable cost, have attracted much attention as materials with unique properties and new application potentials in comparison to the linear polymers.[1,2] Such HBPs possess highly branched structure, high number of end group functionalities, and little entanglements in the melt state, which in turn improve the solubility and enhance the compatibility with other polymers as well as reduce the melt viscosity.[3−7] It is also ready to impart a wide range of structural fine-tuning by adjustment of the degree of branching and/or by functional group modification, which play a significant role in affecting the melt processability and the final physical properties.[7−9] Furthermore, HBPs have somewhat broader molecular weight distribution than the linear polymers and does not exhibit the same dependence of viscosity on the molecular weight; the increase in the viscosity with molecular weight is lower than for the corresponding linear analogues.[10,11] Because of those unique properties, HBPs have been expected to be easily processable without reducing the molecular weight and thus could be very useful as high-solid organic coating agents and polymer rheology control agents/processing aids.[12,13] To explore these ideas, examination and determination of the processability of HBPs are of the first importance, in which the linear viscoelastic behavior and rheological flow properties must be analyzed.

In general, the term processability does not have the same meaning to all the scientists/engineers and does not have objectivity. In addition, its meaning depends not only on the processing equipments but also on the materials to be processed. Therefore, an appropriate method must be employed for a scientific description of the processability. When the specific processing machines and the operating conditions are fixed, temperature, pressure, and the rate and extent of deformation can be estimated. Then, for the specific situation, the material behavior based on the characteristics of the corresponding material governs the processability. Therefore, the appropriate description and a reasonable comparison of the corresponding material behavior serve as a scientific base for the processability. By studying the dynamic mechanical relaxation behavior of the given polymeric materials, the critical information about the material characteristics related to the test of the processability can be extracted. In particular, despite the importance that the molecular mobility can be a direct measure of the degree of processing easiness, few studies have been performed to correlate the molecular mobility with the processability. It is noteworthy that the molecular mobility is generally expressed by the correlation time, τ_c, which is defined as the average relaxation time required for the motional events.[14] The correlation times which characterize the molecular motions in polymers usually fall within a range that typically covers 13 decades of time, $10^{-9} < \tau_c < 10^4$ s.[15] Thus, the wide range of τ_c points out the large differences as to what technique is employed to measure it. The τ_c has been obtained primarily by three relaxation techniques:[15,16] nuclear magnetic resonance (NMR) relaxation, dielectric relaxation, and dynamic mechanical relaxation. NMR relaxation reflects the modulation

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events of magnetic dipoles, which are on a local scale and of a relatively low energy. Thus, the τ_c is several orders of magnitude shorter than that for dielectric or dynamic mechanical relaxation. Dielectric relaxation is limited to detecting the mobility only for the electric dipole of the chemical bonds in the backbone. Dynamic mechanical relaxation measures the whole complex of intermolecular interactions that contribute to the macroscopic modulus, which are important in the melt processing. Therefore, the molecular mobility analysis by the dynamic mechanical relaxation provides a more realistic and promising tool for the evaluation of the processability.

In the present paper, fluoro-terminated hyperbranched poly(ether ketone) (FHBPEK) and its linear analogous poly(ether ketone) (LPEK), possessing both chemical structure and molecular weight similar to those of FHBPEK, were synthesized. FHBPEKs with different degrees of branching were also prepared and referred to as FHBPEK−CM01 and −CM02, in which the degree of branching was controlled by introducing core molecules (mol % of 1.9 and 3.4, respectively) to the extent of little variation in the number-average molecular weights of the three FHBPEKs. The focal point of this study is how to describe and evaluate the processability of hyperbranched polymers from both the scientific and practical point of view, mainly concerning with the molecular mobility aspect of the dynamic mechanical relaxation. Further interest is the effects of the hyperbranched structure vs analogous linear structure and those of the degree of branching on the processability.

Experimental Section

General Measurements. Infrared spectra were recorded on a Perkin-Elmer spectrometer as thin films on KCl disks. ^{1}H NMR spectra were obtained on solutions in dimethyl sulfoxide-d_6 on a Varian VXR 200 (200 MHz for ^{1}H) spectrometer with the TMS proton signal as an internal standard. ^{19}F NMR spectra were recorded on solutions in dimethyl sulfoxide-d_6 on a Varian VXR 200 spectrometer (188.1 MHz for ^{19}F) with the $CFCl_3$ signal as the standard. Gel permeation chromatography (GPC) was carried out on a Waters chromatograph connected to a Waters 410 differential refractometer. 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 resulting GPC data based on the calibration with the polystyrene standard of known molecular weight and polydispersity index. Glass transition temperatures (T_g) were recorded on a Perkin-Elmer DSC-7 with the heating rate of 20 °C/min.

Synthesis. 3,5-Difluoro-4′-methoxybenzophenone, 1. 3,5-Difluorobenzoyl chloride (10 g, 56.6 mmol) in 1,2-dichloroethane (15 mL) was added dropwise to a mixture of anisole (7.6 g, 70 mmol) and aluminum chloride (9.7 g, 73 mmol) in dry 1,2-dichloroethane (30 mL). The mixture was stirred and allowed to react at room temperature under argon for 4 h. Then, water (20 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 ethanol to give the methoxybenzophenone, **1**, as a white solid: 93%; mp 88−89 °C. The structural verification has been described elsewhere.[17]

3,5-Difluoro-4′-hydroxybenzophenone, 2. A mixture of methoxybenzophenone (**1**) (10 g, 40.3 mmol), glacial acetic acid (90 mL), and 48% HBr (60 mL) was heated at reflux for 8h. The reaction mixture was cooled and evaporated to dryness, water (400 mL) was added, and the mixture was extracted with ether (3 × 150 mL). The combined extracts were dried and evaporated to dryness. Then, 0.01N NaOH solution was added to the crude product for the removal of the unreacted methoxybenzophenone. The phenol, **2**, also soluble in the NaOH solution, can be obtained by filtering the mixture and precipitating in 0.01N HCl solution. The crude product was then recrystallized in ethanol to give the phenol, **2**, as a white solid: 85%; mp 138−139 °C. The structural verification has been described elsewhere.[17]

Preparation of Fluoro-Terminated Hyperbranched Poly(ether ketone) (FHBPEK), 3. A mixture of **2** (3 g, 12.8 mmol), dry *N*-methylpyrrolidone (20 mL), dry toluene (15 mL), and potassium carbonate (2.8 g) was heated and allowed to react at reflux under argon for 3h, with the water being collected in a Dean−Stark trap. After this time, the reaction mixture was heated at the stepwise rate of 2 °C/min, and the distillate was collected and removed until the temperature of the reaction mixture had reached ca. 200 °C. Stirring and heating was then continued for another 2.5h. The reaction mixture was poured into water (800 mL), and the precipitate was filtered off and washed with methanol (500 mL × 2). This resulted in the fluoro-terminated hyperbranched poly(ether ketone), **4**, as a white solid: 92% yield. The structural details have been shown elsewhere.[17]

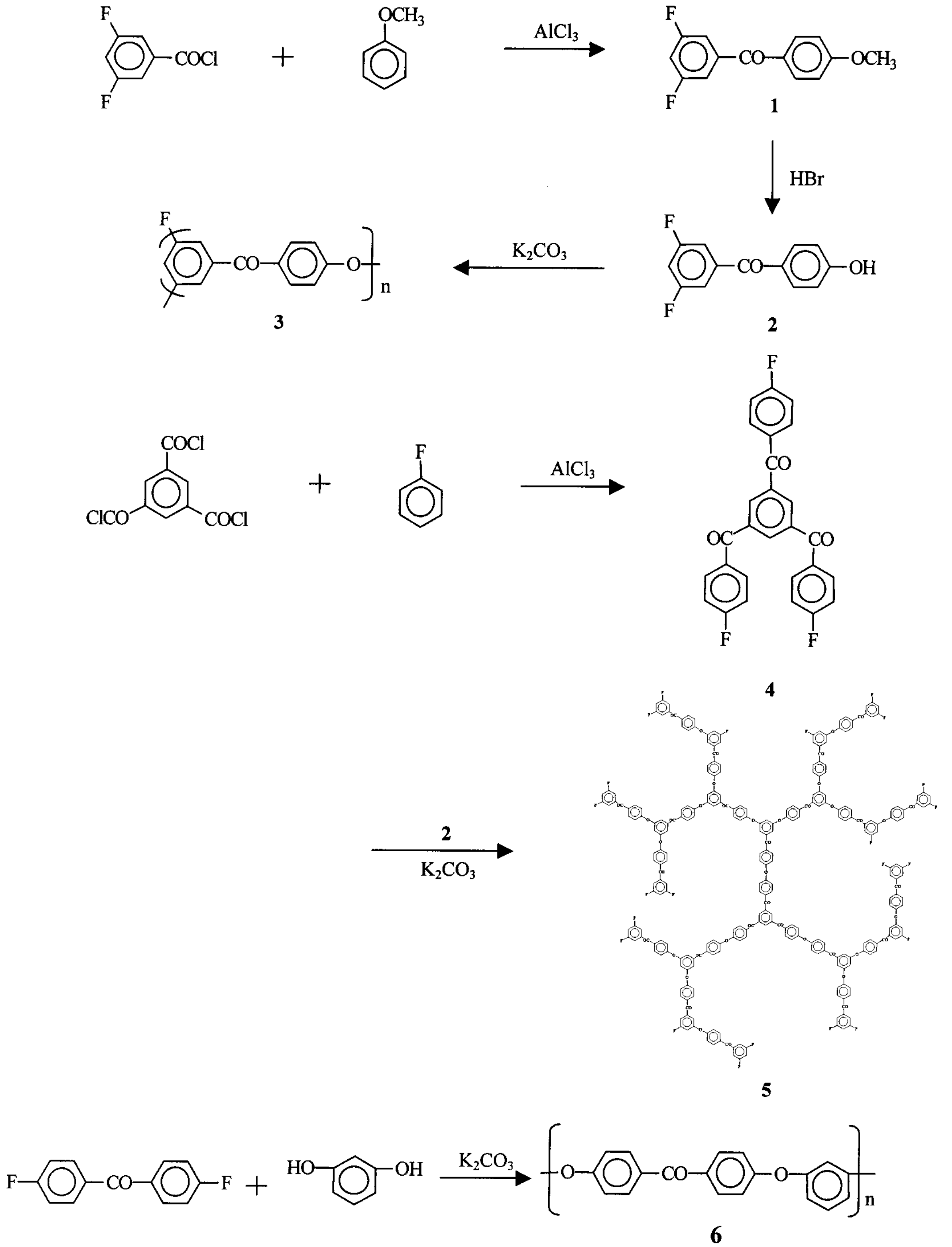
Core Molecule, 4. To a mixture of fluorobenzene (4.5 g, 46.8 mmol) and aluminum chloride (6.7 g, 50 mmol) in dry 1,2-dichloroethane (20 mL) was added dropwise 1,3,5-benzenetricarbonyltrichloride (5 g, 18.8 mmol) in 1,2-dichloroethane (10 mL). The reaction mixture was stirred at room temperature under 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 3200−3000, 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) Having Core Moiety (FHBPEK−CM), 5. Two FHBPEK−CMs were prepared from **2** (3 g, 12.8 mmol) and **4** (0.100 g, 0.225 mmol and 0.200 g, 0.450 mmol, respectively) 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, 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, 1600, 1300, 1210 cm^{-1}.

Frequency-Sweep Dynamic Mechanical Measurements. The dynamic mechanical properties of three FHBPEKs and a LPEK were measured with a Rheometrics RMS-800 mechanical spectrometer. The measurements were performed in shear oscillatory mode using 25 mm-diameter parallel disk geometry with gap setting of ca. 2 mm. The range of angular frequency was from $\omega = 10^{-1}$ to 10^2 rad s^{-1} and the range of temperature was selected from 145 to 250 °C, depending on the sample. The lowest temperature of the measurements was limited by the slippage between the sample and the disk, whereas the highest temperature was limited by thermal degradation. The strain amplitude of 2% was selected to be large enough for accurate torque signals and small enough to keep the material response in the linear region. The dynamic mechanical data were obtained as a function of temperature above 10 or 20 °C higher than the calorimetric T_g determined by DSC. For FHBPEKs, it was rather difficult to measure the dynamic mechanical properties of FHBPEKs near their corresponding T_g's because the very high torque was resulted at these temperatures. It is noteworthy that the polymers subjected to the dynamic mechanical measurement may soften at the temperatures higher than those of the calorimetric T_g in general, owing to the differences in the time scale between the two methods.

Scheme 1



Results and Discussion

Synthesis and Characterization. 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 a reaction developed by Hawker.[17] The synthesis recipe and the purification method were selected, considering the accessibility to the dynamic mechanical measurements wherein multigram yields are usually required. To investigate and compare the role of the hyperbranched structure against the linear analogous one, the linear poly(ether ketone) (LPEK), **6**, whose chemical structure and molecular weight are similar to those of **3**, was prepared from 4,4′-difluorobenzophenone and resorcinol in the presence of K_2CO_3 in NMP at reflux for 3 h in 95% yield (Scheme 1). The resorcinol used 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. Furthermore, to vary the degree of branching of FHBPEK, the core molecule **4** was synthesized by Friedel−Crafts acylation reaction in 71% yield. Polymerization of **2** with different mole ratio of **4** (mol % of 1.9 and 3.4, respectively) in the presence of K_2CO_3 in NMP at 150−200 °C for 6 h produced two FHBPEKs (FHBPEK−CM01 and −02, respectively), **5**, having different degrees of branching.

Molecular weights of the three different FHBPEKs and the LPEK were determined by GPC analysis

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	degree of branching	T_g (°C)
FHBPEK	100/0	14 500	15.0	0.49	145
FHBPEK−CM01	57/1	12 300	8.0	0.62	138
FHBPEK−CM02	28/1	11 000	2.5	0.67	130
LPEK		15 400	1.4		123

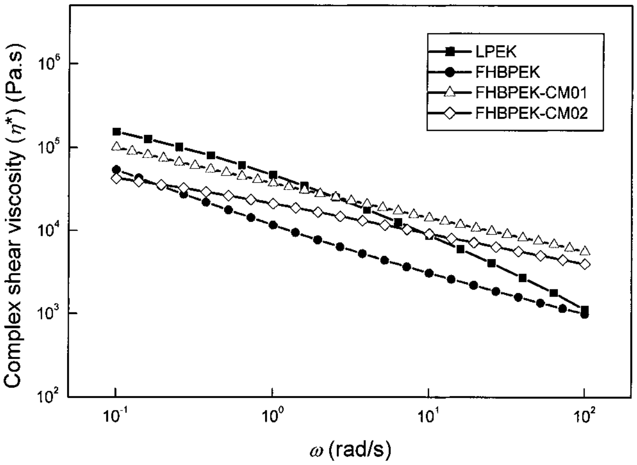


Figure 1. Complex shear viscosity η^* of LPEK (■), FHBPEK (●), FHBPEK−CM01 (△), and FHBPEK−CM02 (◇) as a function of angular frequency at a fixed temperature, T_g + 45 °C.

calibrated with linear polystyrene standards. Hyperbranched polymers are generally expected to exhibit the lower molecular weight in comparison with their linear analogues.[18] This is mainly ascribed to the smaller hydrodynamic volume decreased by the high branching than for its linear counterpart of the same molar weight. The results of the number-average molecular weights and the polydispersity index for FHBPEKs and LPEK are shown in Table 1. The molecular weights of LPEK measured by GPC are somewhat higher than those of FHBPEKs. However, owing to the hydrodynamic volume effects of FHBPEKs, the actual molecular weight of FHBPEKs would be similar or slightly higher than that of LPEK. Differential scanning calorimetry (DSC) was used to characterize the thermal transitions. Shorter branches of FHBPEK−CM01 and −CM02, increasing the degree of branching, probably cause the decrease of T_g's, compared to that of FHBPEK. Another important material characteristic of describe the structural features of the hyperbranched polymers is the degree of branching (DB). Unlike dendrimers that are perfectly branched and have a DB of 100%, hyperbranched polymers accept a certain degree of imperfection; i.e., the values of the DB were anywhere between 0% and 100%. The DB of a hyperbranched polymer is commonly calculated according to the following equation:[19]

$$\mathrm{DB} = \frac{D + T}{D + T + L} \tag{1}$$

D, *T*, and *L* are the fractions of dendritically, terminally, and linearly incorporated monomer units in the hyperbranched polymer. For high molecular weights, the sum of terminal and dendritic units becomes practically identical since the number of dendritic units is theoretically equal to that of terminal units plus one. Thus, the eq 1 can be modified as[20]

$$\mathrm{DB} = \frac{2T}{2T + L} \tag{2}$$

The FHBPEKs include a terminal unit with two fluorine groups and a linear unit with one fluorine group. The chemical environments of terminal and linear fluorine groups are different, allowing the relative proportion to be evaluated by ^{19}F NMR spectroscopy. From the spectra of ^{19}F NMR spectroscopy, the resonance peak at −108.3 ppm can be assigned as the linear unit, while the peak at −107.7 ppm is due to the terminal unit. The DBs of FHBPEKs were determined using the values of the relative percentage of terminal and linear units obtained from integration of the respective signals in ^{19}F NMR spectra (also see Table 1). More details for the determination of DBs of the FHBPEKs have been described in the series of our study.[21]

Rheological Behavior, Molecular Mobility, and Melt Processability. Figure 1 represents the complex shear viscosity $\eta^*(\omega)$ of FHBPEKs and LPEK as a function of angular frequency ω at the corresponding temperatures uniformly higher by 45 °C than their respective T_g's, all of them being in the molten state. From empirical interrelations between shear functions, called the Cox−Merz rule, the shear rate dependence of the steady-state viscosity η is equal to the frequency dependence of the linear viscoelastic viscosity η^*.[22] Thus, the Newtonian or non-Newtonian behavior of FHBPEKs and LPEK can be estimated by the η^* vs ω plots. From the slopes of the plots, FHBPEKs showed linearity whereas LPEK nonlinearity and only a small decrease in viscosity with increase of frequency in the range 10^{-1}−10^2 rad s^{-1}. As the degree of branching increased, the slope and dependence of $\eta^*(\omega)$ on frequency decreased gradually. This observation indicates that the rheological behavior of FHBPEKs followed more similarly that of a Newtonian fluid, which was more prominent for the higher degree of branching, and the amount of entanglements between polymer chains was accordingly decreased. The latter was confirmed by comparing the frequency-scan dynamic mechanical behavior, Figures 2−4. The rubbery plateau region could be detected in FHBPEK, and this region was shown to decrease as the degree of branching increased. Moreover, the junction point of the shear storage modulus, $G'(\omega)$ and the shear loss modulus, $G''(\omega)$ occurred between the glass−rubber transition and the rubbery plateau was observed in FHBPEK and FHBPEK−CM01. For both FHBPEK and FHBPEK−CM01, the $G'(\omega)$ values at the frequencies below that of the junction point were higher than the $G''(\omega)$ values, which was one of the characteristics implying the presence of the rubbery plateau region. On the contrary, in FHBPEK−CM02 where the values of $G''(\omega)$ were all above those of $G'(\omega)$, the rubbery plateau region and the crossover were not present within the whole experimental range of temperatures. From the dynamic mechanical studies, a novel melt behavior was investigated that a Newtonian-like flow, i.e., a small entanglement effect of FHBPEK series, could be seen only above the critical value of degree of branching, probably >0.62−0.67.

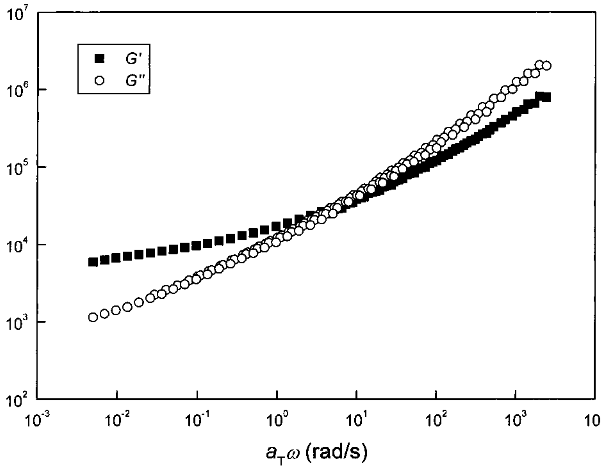


Figure 2. Master curve of the dynamic moduli G' (■) and G'' (○) for FHBPEK, representing the behavior over an extended frequency scale at the reference temperature of 190 °C.

Below that value, the FHBPEKs started to develop a crossover of the $G'(\omega)$ and $G''(\omega)$ curves and a rubbery plateau region. Further investigations of the end group functionality effects on the rheological behavior will be in a future publication.

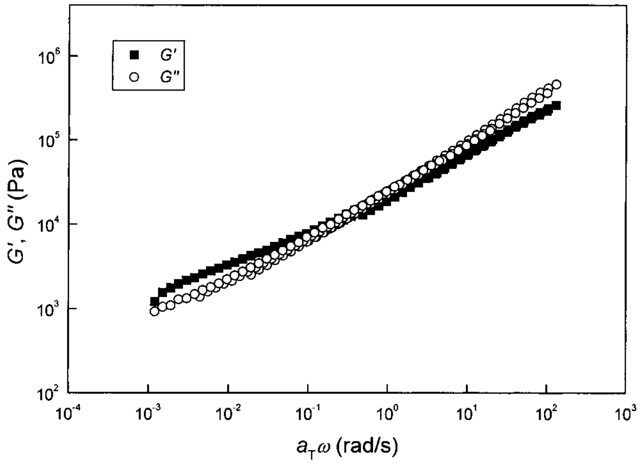


Figure 3. Master curve of the dynamic moduli G' (■) and G'' (○) for FHBPEK−CM01, representing the behavior over an extended frequency scale at the reference temperature of 190 °C.

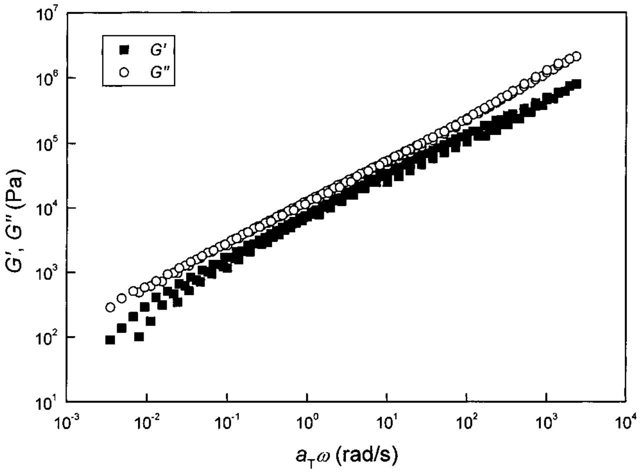


Figure 4. Master curve of the dynamic moduli G' (■) and G'' (○) for FHBPEK−CM02, representing the behavior over an extended frequency scale at the reference temperature of 190 °C.

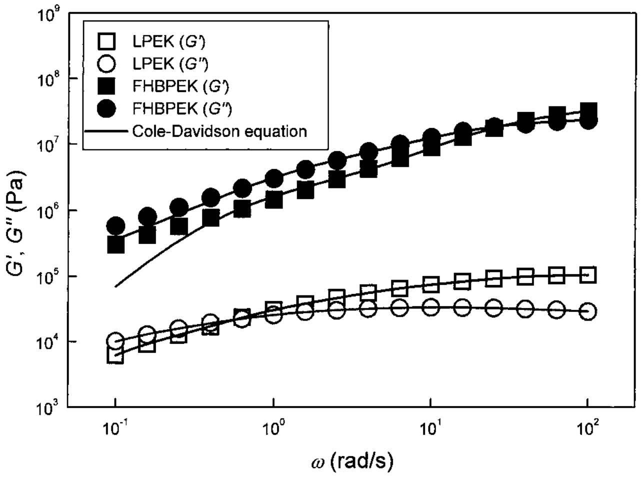


Figure 5. G' (□) and G'' (○) of LPEK and the G' (■) and G'' (●) of FHBPEK as a function of angular frequency at 170 and 165 °C, respectively. The solid lines are the fits to the real and imaginary parts of eq 4, respectively.

Both the dynamic moduli $G'(\omega)$ and $G''(\omega)$ of three FHBPEKs and a LPEK as a function of temperature near and above T_g can be used to obtain a quantitative measure of their corresponding molecular mobility, and to evaluate their melt processability in terms of the molecular mobility. It has been well-known the relaxation behavior of polymer melts follows an exponential relaxing process not with only a single relaxation time but with a distribution of the relaxation times.[23] Thus, the dynamic mechanical data must be treated with empirical fitting functions in order to represent the relaxation behavior and determine the single average relaxation time. One of such empirical fitting functions with widespread acceptance is the Cole−Davidsion distribution function of relaxation times.[24] The Cole−Davidson function has been originally derived to fit the dielectric relaxation data, and can be also used to analyze the dynamic mechanical relaxation data by appropriately changing the variables from the dielectric to the dynamic mechanical, considering the general relationships have been found between them. The empirical Cole−Davidson equation is given by

$$G^*(\omega) \approx G_\infty\left(1 - \frac{1}{(1 + i\omega\tau_{\mathrm{C-D}})^{\beta_{\mathrm{C-D}}}}\right) \qquad (4)$$

where $G^*(\omega)$ is the complex shear modulus, G_∞ is the high-frequency limiting storage modulus, $\tau_{\mathrm{C-D}}$ is the Cole−Davidson relaxation time implying a maximum relaxation time present in the system, and the $\beta_{\mathrm{C-D}}$ is the Cole−Davidson width parameter.[25,26] Considering a real and an imaginary part of $G^*(\omega)$ as $G^*(\omega) = G'(\omega) + iG''(\omega)$, nonlinear curve fitting is performed on both $G'(\omega)$ and $G''(\omega)$ data to obtain $\tau_{\mathrm{C-D}}$, $\beta_{\mathrm{C-D}}$, and G_∞. In Figure 5, the $G'(\omega)$ and $G''(\omega)$ of FHBPEK and LPEK are shown to fit by the Cole−Davidson function, respectively. Then, the average relaxation time, $\langle\tau_{\mathrm{C-D}}\rangle$, that is, the correlation time, τ_c, can be determined from the distribution of relaxation times to be $\tau_c = \langle\tau_{\mathrm{C-D}}\rangle = \tau_{\mathrm{C-D}}\beta_{\mathrm{C-D}}$.[26] The correlation times, τ_c's, of three FHBPEKs and an LPEK as a function of temperature are shown in Figure 6. As the degree of branching of FHBPEKs increased, the τ_c values became shorter, and hence the molecular mobility increased at the corresponding temperature range. In addition, the FHBPEKs exhibited faster molecular motion than their linear

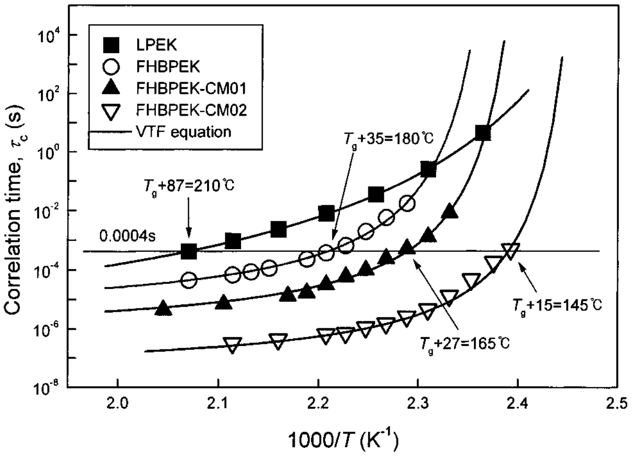


Figure 6. Correlation times, τ_c's, for LPEK (■), FHBPEK (○), FHBPEK−CM01 (▲), and FHBPEK−CM02 (▽) as a function of temperature. The solid lines are the fits to eq 5.

counterparts through the temperatures. It has been reported that the optimum temperature for the melt processing of the polymers lies typically in a range of 50−100 °C above the T_g.[23] Thus, the τ_c of LPEK at 87 °C at which the polymer is considered to be in the optimum temperature range for the melt processing was 0.0004 s. For the FHBPEK, however, the same τ_c (i.e., 0.0004 s) is reached even at $T_g + 35$ °C only, compared to the LPEK at $T_g + 87$ °C. This result indicates that the FHBPEK is melt processable at a temperature of 52 °C lower than the LPEK. The FHBPEK−CM01 and −CM02 exhibited the same τ_c even at lower temperatures, i.e., $T_g + 27$ °C and $T_g + 15$ °C, respectively. From these results, the hyperbranched polymers indicate the superior melt processability in comparison to their linear analogue. Moreover, with increase of the degree of branching the optimum temperature range for the melt processing is dramatically reduced, which plays a crucial role in enhancing the melt processability.

Further insights into Figure 6 by fitting the τ_c's to the Vogel−Tamman−Fulcher (VTF) equation and the Arrehnius-type equation provided novel information about the temperature dependence of the molecular motion and the activation energy of the hyperbranched polymers with different degree of branching, in conjunction with their processability. The solid lines in Figure 6 are the fits of the τ_c's to the VTF equation

$$\tau_c = A \exp\left(\frac{DT_0}{T - T_0}\right) \qquad (5)$$

where A and D are material parameters and T_0 is the temperature where a special singularity in dynamics is anticipated in that viscosity and relaxation times approach infinity.[27,28] From the VTF equation extrapolation, the dynamic-mechanically determined T_g can be obtained as taking the temperature at which the τ_c attains a theoretically expected long time, e.g., 100 s.[29] As summarized in Table 2, the dynamic mechanical T_g's were higher than the calorimetric T_g's, and the difference between them is more prominent for the LPEK. From these results, it is conjectured that the chain molecules of the hyperbranched polymer respond more similarly to the thermal and mechanical stimuli than the linear polymer. Referring to the Figure 6 and the τ_c values just above and below the dynamic mechanical T_g (i.e., at $T_g + 1$ °C and at $T_g - 1$ °C) in Table 2, the molecular mobility and the processability at the temperatures above the mechanical T_g was higher in the order FHBPEK−CM02, −CM01, FHBPEK, and LPEK. However, as the temperature decreased below the T_g the molecular mobility became totally reversed, in the order FHBPEK−CM02, −CM01, FHBPEK, and LPEK from lower to higher. In VTF equation, the parameter D indicates the deviation from the Arrhenius law and the fragility of the materials. The more fragile the material, the more deviation from the Arrhenius law and the smaller D value (typically $D < 10$). As listed in Table 2, the D values of the FHBPEKs were smaller than the LPEK and decreased with increase of the degree of branching, implying that the branching structure induced the fragility in the materials.

Table 2. Apparent Activation Energy, T_g, and Material Parameter D of Hyperbranched Poly(ether ketone)s and Linear Counterpart

	apparent activation energy (kJ/mol)			
sample	high-temperature region	low-temperature region	T_g (°C)[a]	D
FHBPEK	80	465	153	1.9
FHBPCM01	64	476	149	1.1
FHBPCM02	47	492	137	0.7
LPEK	320 (single fitting)		142	2.8

[a] By VTF extrapolation.

The processability evaluation and the temperature dependence of the molecular mobility are further confirmed by analyzing the apparent activation energy, E_a, determined by a curve fitting of the τ_c's to the following Arrehnius equation:

$$\tau_c = \tau_{c,o} \exp(E_a/RT) \qquad (6)$$

$\tau_{c,o}$ is the preexponential factor, and R is the gas constant. The LPEK was fit by a single-component function whereas fitting of all the three FHBPEKs were resolved into two components approximately before and behind the point at their respective calorimetric $T_g + 30$ °C. As shown in Table 2, the apparent activation energies of the three FHBPEKs in the temperature range above their calorimetric $T_g + 30$ °C were lower compared to that of the LPEK and became reduced as the degree of branching increased. In contrast, at temperatures lower than their calorimetric $T_g + 30$ °C the activation energies of the FHBPEKs were much higher than the LPEK and also increased with the degree of branching. These tendencies were in good agreement with that of the τ_c's analyzed by the VTF equation extrapolation and can be explained by the following aspects. The higher degree of branching in the FHBPEKs made the branches shorter and the structures more globular, which caused the denser packing of the chain molecules especially at the chain ends. The densely packed molecules of the FHBPEKs resulted in the high τ_c's and required the more energies to activate the motion in the temperature range below their respective $T_g + 30$ °C. However, increase of the temperature above their $T_g + 30$ °C should easily generate the molecular motion of the FHBPEKs because there were more mobile shorter branches and little entanglements, which was comparable to the LPEK possessing a considerable amount of the entanglements.

Conclusions

In the present paper, three fluoro-terminated hyperbranched poly(ether ketone)s (FHBPEK, FHBPEK-01, FHBPEK-02) with different degrees of branching and their linear analogous poly(ether ketone) (LPEK) whose chemical structure and molecular weights were similar to those of FHBPEKs were prepared and compared.

1. The degrees of branching were controlled by the amount of using the core molecules, resulting in 0.49 for FHBPEK, 0.62 for FHBPEK−CM01, and 0.67 for FHBPEK−CM02) with little variation in the number-average molecular weights of the three FHBPEKs.

2. From the dynamic mechanical analyses, nonentangled molecular structure and a Newtonian-like flow behavior of FHBPEKs could be observed only above a certain critical value (>0.62−0.67) of the degree of branching, where the crossover of the storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$ started to disappear.

3. The correlation time, τ_c, was determined from the shear relaxation moduli and the Cole−Davidson equation, which provided a unique means to evaluate the melt processability on the basis of the molecular mobility. Highly branched structures of FHBPEKs predominantly increased the molecular mobility and enhanced the melt processability, realizing the optimum processing temperature lowered by 52−72 °C depending on the degree of branching, compared to that of LPEK.

4. Nonlinear curve fittings of the correlation times with the Vogel−Tamman−Fulcher (VTF) equation and the Arrhenius equation provided some novel information about temperature dependence of the molecular mobility and the activation energy, in conjunction with the processability and the fragility of the FHBPEKs in comparison to the LPEK. The more highly branched structure generated the faster molecular motion and the less activation energy above T_g, contributing to the better processability. In contrast, below T_g the slower molecular motion and the much more activation energy were caused by the hyperbranched structure with the higher degree of branching, possibly due to the more densely packed molecules originated from the shorter branches and more globular geometry. Furthermore, the hyperbranched polymers showed a more deviation from the Arrhenius relation, an indicative of the more fragile amorphous materials, as the degrees of branching increased.

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