5284 *Macromolecules* **2007,** *40,* 5284−5289

Synthesis and Chemical, Physical, and Optical Properties of 9,9-Diarylfluorene-Based Poly(ether−ether−ketone)

Shinichi Kawasaki,[†] Masahiro Yamada,[†] Kana Kobori,[†] Fengzhe Jin,[‡] Yoshikazu Kondo,[‡] Hideki Hayashi,[§] Yuichi Suzuki,[§] and Toshikazu Takata*,[§]

Advanced Material Business Promotion Department, Osaka Gas Co., Ltd., Konohana, Osaka 554-0051, Japan; Advanced Materials Research Laboratory, KRI Incorporated, Shimokyo-Ku, Kyoto 600-8813, Japan; and Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Ookayama, Meguro, Tokyo 152-8552, Japan

Received March 11, 2007; Revised Manuscript Received May 18, 2007

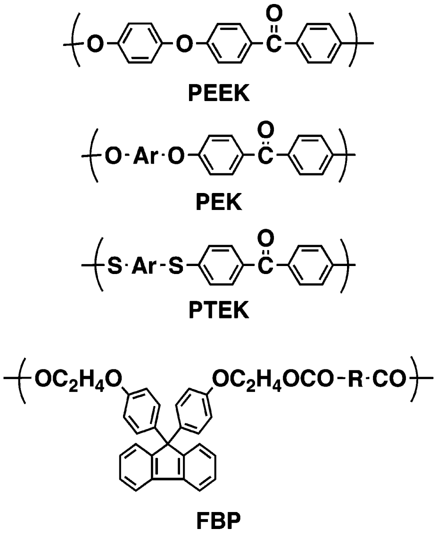
ABSTRACT: Fluorene-based poly(ether−ether−ketone) (F-PEEK) was designed and synthesized by reacting a 9,9-diarylfluorene-containing biphenol and a naphthalene-containing dihaloarene. High molecular weight F-PEEK ($M_w > 270\,000$; $M_n \sim 55\,000$) was obtained in quantitative yields by the two-step polycondensation of 9,9-bis-(4-hydroxy-3-methylphenyl)fluorene and 1,5-bis(4-fluorobenzoyl)-2,6-dimethylnaphthalene in the presence of cesium carbonate in diphenyl sulfone at 165 °C and then 220 °C. The chemical, physical, and optical properties of F-PEEK were evaluated. Good solubility of F-PEEK in ordinary organic solvents such as THF and chloroform was confirmed. F-PEEK exhibited a high refractive index of 1.64 at 589 nm, whereas it showed a much lower birefringence value than a polycarbonate or a polyester. F-PEEK was amorphous and transparent at room temperature. The transmittance of F-PEEK in film state was over 80% in the visible region. These optical properties were probably related to the *cardo* structure of the fluorene moiety placed on the main chain. No phase transition except for T_g was confirmed in the DSC analysis. F-PEEK displayed a high storage modulus ($E' = 2.93$ GPa) and glass transition temperature (280 °C) in comparison with commercially available poly(ether−ether−ketone) (PEEK, $E' = 1.73$ GPa and T_g 169 °C). The high modulus of F-PEEK was derived unambiguously from both the fluorene and naphthalene skeletons.

Introduction

Poly(ether−ether−ketone) (PEEK, Scheme 1) is one of the highest performance thermoplastics characterized not only by outstanding thermal, chemical, and mechanical properties but also by nonflammable properties and good processability. Therefore, PEEK has been used in the fields of electronics, automobile, chemical engineering, and others.[1−5] However, PEEK exhibits low T_g and high crystallization speed resulting in nontransparent opaque materials and limiting its use in the optical and display fields where transparency of materials is required. Takata et al. previously reported the synthesis of novel transparent poly(ether−ketone)s (PEKs) showing high solubility and thermal stability by polycondensation using 1,5-bis(4-halobenzoyl)-2,6-dimethylnaphthalene as dihaloarene.[6−8] Further, corresponding sulfur analogues poly(thioether−ketone)s (PTEKs) have also been reported to have similarly good properties in addition to inflammable and thermosetting properties.[9−12]

Nevertheless, the *cardo* structure caused by the 9,9-diarryl-substituted fluorene skeleton is of significance in polymers for optical use. A 9,9-diarylfluorene-based amorphous transparent polyester (Figure 1, FBP), which is characterized by a high refractive index and a low birefringence, is currently used as optical material.[13] Some other characteristic properties including fine dispersing ability for filler and high thermal stability of FBP have also been demonstrated.[14−21] On the basis of these observations, we have recently designed a novel type of 9,9-diarylfluorene moiety-containing PEEK (F-PEEK) combining nonplanar naphthalene-based dihaloarene and "*cardo*" 9,9-diarylfluorene-based biphenol. This paper discloses the synthesis of F-PEEK as a high performance polymer with exceptional chemical, thermal, and optical properties.

Scheme 1



Experimental Section

Spectroscopic Measurement and Molecular Weight Evaluation. IR spectra were recorded on a JASCO FT/IR-460 Plus. ^{1}H NMR spectra were obtained with a JEOL JNM-AL 400 spectrometer (400 MHz), and chemical shifts were calibrated using tetramethylsilane as internal standard. The fluorescence spectrum was recorded in $CHCl_3$ on a JASCO FP-6500. The UV spectrum in $CHCl_3$ was obtained with a JASCO V-550. Molecular weight and

---

* Corresponding author. E-mail: takata.t.ab@m.titech.ac.jp.

[†] Osaka Gas Co., Ltd.

[‡] KRI Incorporated.

[§] Tokyo Institute of Technology.

10.1021/ma070589n CCC: $37.00

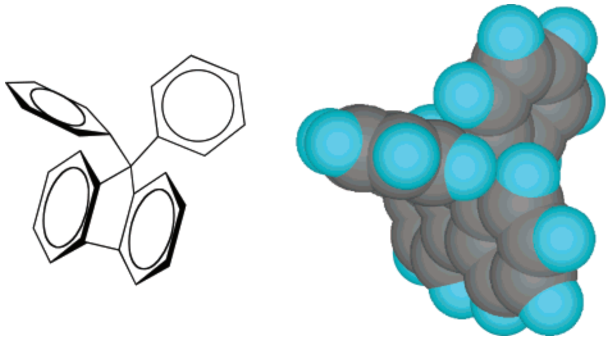


Figure 1. *Cardo* structure of 9,9-diphenylfluorene: chemical (left) and MM2 simulated (right) structures.

its distribution were estimated by GPC on a JASCO Gulliver system equipped with two consecutive linear polystyrene gel columns (Tosoh TSKgel G5000H$_{XL}$, G4000H$_{XL}$) at 30 °C (flow rate 0.085 mL/min) using polystyrene standards and chloroform as an eluent. Thermogravimetric analysis (TGA) was performed on a Shimadzu TGA- 50 instrument at a heating rate of 10 °C/min under a N_2 atmosphere (flow rate of 50 mL/min) to determine decomposition temperature T_{d5} at which 5% weight loss was observed. Differential scanning calorimetry (DSC) was carried out using a Shimadzu DSC-60 instrument at a heating rate of 10 °C/min under a N_2 atmosphere (flow rate of 50 mL/min) to determine the glass transition temperature T_g.

Materials. Commercially available 9,9-bis(3-methyl-4-hydroxyphenyl)fluorene (DFA), diphenyl sulfone (solvent), and cesium carbonate were obtained from Osaka Gas Chemical, Aldrich, and Wako Chemicals, respectively, and used without further purification. The synthesis of 1,5-bis(4-fluorobenzoyl)-2,6-dimethylnaphthalene (BHA) was achieved by the reported method.[6−8] Commercially available PEEK (Mitsui Chemicals Co., Ltd., 450G), polyethylene telephthalate (PET, Mitsubishi Chemical Corp., DiaPET MA 521), and polycarbonate (PC, Teijin Chemicals Ltd. AD-550) were used without further purification except drying. PEEK, PET, and F-PEEK were dried in an oven at 110 °C for 7 h before use.

Synthesis of F-PEEK. A mixture of 9,9-bis(3-methyl-4-hydroxyphenyl)fluorene (1.14 g, 3.00 mmol), 1,5-bis(4-fluorobenzoyl)-2,6-dimethylnaphthalene (1.20 g, 3.00 mmol), diphenyl sulfone (12 g), and cesium carbonate (2.93 g, 9.00 mmol) were heated with stirring at 160 °C for 2 h and then at 220 °C for an additional 2 h in a round-bottom flask under argon. The reaction mixture was cooled to room temperature. The mixture was poured into 200 mL of chloroform to dissolve the reaction products, and the resulting mixture was precipitated into 1.5 L of methanol. The white precipitates were collected by filtration, washed with methanol, water, and acetone, and vacuum-dried to give a white powdery polymer (yield 2.15 g, 99%). M_w 270 000, M_n 55 000, M_w/M_n 4.90 by GPC; T_g 280 °C by DSC; T_{d5} 454 °C by TGA. IR (KBr): 3058 (m), 3036 (m), 3023 (m), 2952 (w), 2921 (m), 2860 (w), 1665 (s), 1593 (s), 1491 (s), 1447 (m), 1416 (m), 1387 (m), 1335 (w), 1304 (m), 1248 (s), 1220 (s), 1153 (s), 1119 (s), 1033 (w), 1010 cm^{-1} (w). ^{1}H NMR ($CDCl_3$): δ 7.77 (d, 2H, $J = 7.6$ Hz, fluorene ArH), 7.8−7.7 (m, 4H, benzoyl ArH), 7.46 (d, 2H, $J = 8.8$ Hz, naphthalene ArH), 7.41 (d, 2H, $J = 7.6$ Hz, fluorene ArH), 7.38 (t, 2H, $J = 7.6$ Hz, fluorene ArH), 7.29 (t, 2H, $J = 7.6$ Hz, fluorene ArH), 7.21 (d, 2H, $J = 8.4$ Hz, naphthalene ArH), 7.1−7.0 (m, 4H, cresol ArH), 6.9−6.8 (m, 6H, benzoyl ArH and cresol ArH), 2.24 (s, 6H, naphthalene Me), 2.05 (s, 6H, cresol Me). Detailed assignment is shown in Figure 2. Synthesis of F-PEEK was carried out under various conditions. Results are summarized in Table 1.

Film Preparation. F-PEEK, PEEK, PC, and PET films were prepared under the pressure of 40 MPa at temperatures of 350, 370, 230, or 270 °C. The pressed films were quenched with ice−water immediately after removal from the hot stage.

Refractive Index. The refractive index of the polymer sample was measured by Abbe refractometer (DR-M2/1550 ATAGO CO., LTD). Because semicrystalline PEEK samples become opaque, the refractive index could not be measured.

Transmittance. The transmittance of F-PEEK and PEEK films was evaluated by UV−vis spectrophotometer (U-3010 HITACHI High Technology) with a scanning range of 200−800 nm.

Birefringence. The birefringence of F-PEEK and PET films was evaluated by taking the pictures of the films placed between two crossing polarizing films. Retardation of lights in F-PEEK, PET, and PC films was measured by polarized optical microscopy (OPTIPHOTO-POL, Nikon, Japan) under the cross-Nicols (546 nm). The samples for the retardation measurement were set to 200 μm thickness.

Thermal Analysis. F-PEEK was pressed at 330 °C under vacuum on a hot plate and quenched to room temperature immediately after removal from the plate. The film samples were further annealed at 300 °C for 20 min. The resulting samples were quenched at 0 °C. The amorphous films made through these processes were annealed at different temperatures. The thermal properties of the films were evaluated by differential scanning calorimetry (DSC, Rigaku Co., Ltd., ThemoPlusDSC8020). The measurement was performed from room temperature to 500 °C at a heating rate of 15 °C/min.

Viscoelastic Measurement. The polymer films (0.1 mm thickness) quenched at 0 °C were used for the dynamic mechanical thermal analysis (DMTA). DMTA measurement was performed on a Rheogel-E4000 (UBM) in tensile mode. The frequency of the measurement was fixed at 10 Hz, and the tension applied to the samples was controlled automatically by the machine, where 3 °C/min heating rate was applied.

X-ray Diffraction Profile. The polymers prepared under the conditions indicated in Figure 8 were further hot-pressed at 350 °C followed by quenching at 0 °C to finally obtain amorphous films (0.1 mm thickness). The films annealed at 250 °C for 30 min were used as crystallized samples. The X-ray diffraction profiles of the samples were measured by a MXP21 (Mac Science Co., Ltd). Cu Kα_1 ($\lambda = 0.154\,056$ nm) X-ray was applied to the measurement which was performed by the reflect method among the 2θ range of 5−50° with an interval of 0.02.

Results and Discussion

Synthesis and Structure of F-PEEK. The synthesis of F-PEEK was carried out by the polycondensation of 9,9-bis-(4-hydroxy-3-methylphenyl)fluorene (BHF) and 1,5-bis(4-fluorobenzoyl)-2,6-dimethylnaphthalene (DFA) in the presence of cesium carbonate as base in diphenyl sulfone as solvent under an argon atmosphere via two-step heating (Scheme 2).

The polymerization was examined under various conditions. Selected results of the polymerization are summarized in Table 1. Table 1 data clearly suggests that a higher temperature results in the formation of higher molecular weight F-PEEK, although

Table 1. Synthesis of F-PEEK from DFA and BHF[a]

run	temp first heat (°C)	time (h)	temp second heat (°C)	time (h)	yield (%)	$M_w{}^b \times 10^3$	$M_n{}^b \times 10^3$	$M_w/M_n{}^b$
1	140	2	200	3	99	81	37	2.2
2	150	2	220	4	99	346	54	6.4
3	165	2	220	2	99	270	55	4.9
4	165	2	220	3	99	319	56	5.7
5	220	5			99	1750	92	19

[a] Polycondensation: a mixture of DFA (3.00 mmol) and BHF (3.00 mmol) was heated in the presence of cesium carbonate (9.00 mmol) in diphenyl sulfone (12 g) (Scheme 2). [b] M_w, M_n, and M_w/M_n were estimated by GPC (polystyrene standards, eluent: chloroform).

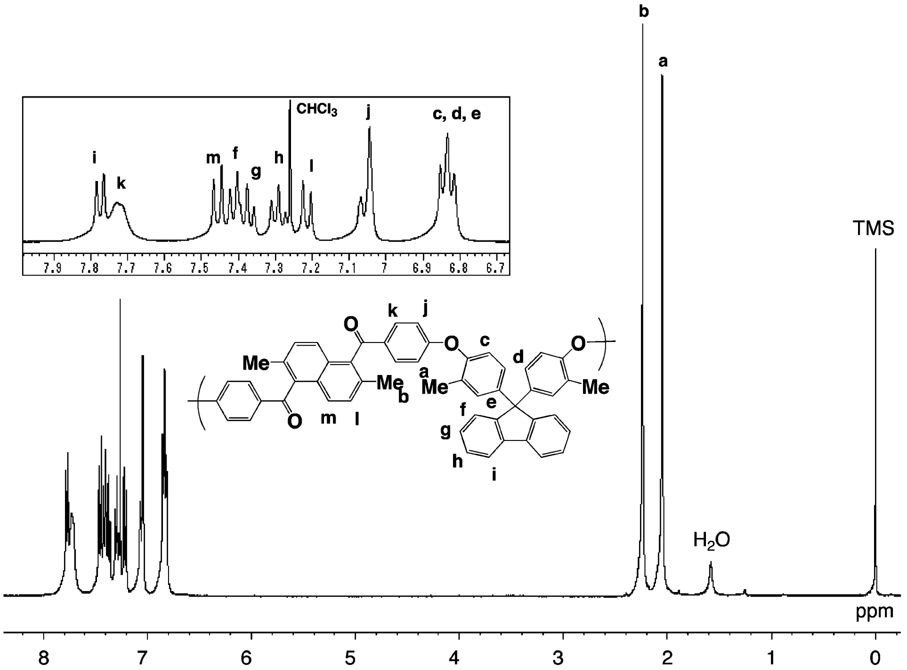
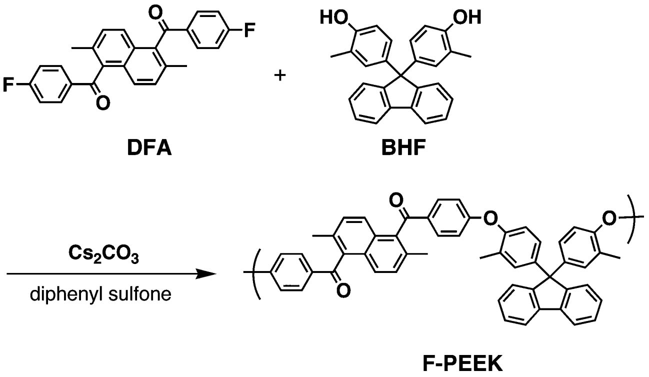


Figure 2. ^{1}H NMR of F-PEEK (M_w 270 000, M_n 55 000, M_w/M_n 4.9) (400 MHz, 298 K, $CDCl_3$) and the signal assignment.

Scheme 2



prolonged reaction time gives wider molecular weight distribution. It was eventually concluded that two-step heating at 165 and 220 °C for 2 and 2 h, respectively, was sufficient to obtain F-PEEK with high molecular weight (e.g., M_w 270 000, M_n 55 000, M_w/M_n 4.9).

Figure 2 indicates the ^{1}H NMR spectrum of F-PEEK (M_n 55 000), which was clearly consistent with the polymer structure. Two kinds of methyl signals around 2.2 ppm appeared in addition to the aromatic signals which were as well assigned as those of F-PEEK in Figure 2 although they were rather complicated. In particular, the markedly sharp signals throughout the spectrum clearly suggested a very low degree of disorder in the polymer structure. Other spectroscopic data such as the IR data unambiguously supported the formation of the poly(ether−ether−ketone) structure (1665 cm^{-1} for C═O, 1593 cm^{-1} for Ar−H, and 1248 cm^{-1} for C−O−C). F-PEEK also had a UV−vis absorption peak around 320 nm and fluorescence absorption around 420 nm based on the nonconjugated structure in the main chain (Figure 3).

Properties of F-PEEK. *Solubility.* Although F-PEEK is constituted mostly of aromatic parts, its solubility is high enough to be dissolved quickly in typical organic solvents such as THF, toluene, dichloromethane, and chloroform, in contrast to PEEK. The unusually high solubility observed here presumably comes from the special structure of 9,9-diarylfluorene and 1,5-diaryl-2,6-dimethylnaphthalene moieties in the main chain, as discussed in the Introduction. Thin films were easily obtained by casting the F-PEEK solution in an organic solvent like chloroform, dichloromethane, or THF onto a Teflon plate.

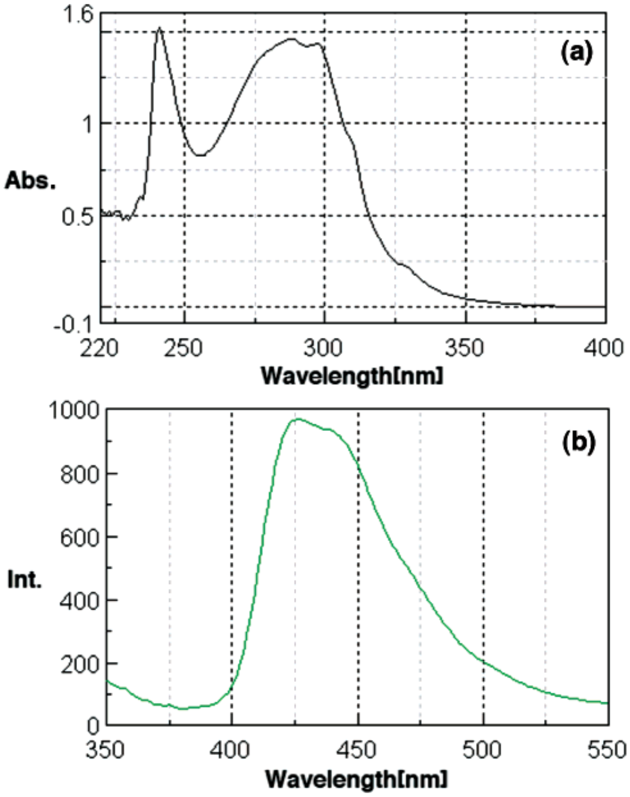


Figure 3. UV−vis (a) (THF, [C] = 2.5 × 10^{-4} M, 298 K) and fluorescence (b) (THF, [C] = 2.5 × 10^{-4} M, 298 K) spectra of F-PEEK.

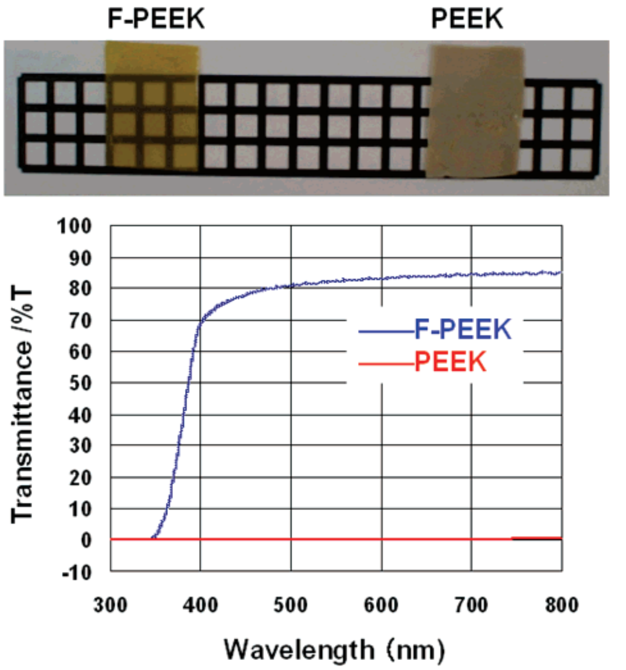


Figure 4. Transmittance of PEEK and F-PEEK obtained by the measurement in a scanning width ranging from 200 to 800 nm with a UV−vis spectrophotometer.

Table 2. Wavelength-Dependent Refractive Index of F-PEEK

wavelength (nm)	refractive index	wavelength (nm)	refractive index
656	1.634	486	1.671
589	1.646	436	1.690
546	1.656		

Transparency. Although PEEK was opaque due to its semicrystalline nature, F-PEEK was sufficiently transparent at room temperature (Figure 4). The transmittance gradually increased with the increase of wavelength of visible light. In the range of 500−800 nm the transmittance reached over 80%. The transparency of F-PEEK probably results from its amorphous nature presumably owing to both the *cardo* structure of the fluorene moiety and the nonplanar structure of the naphthalene moiety in the main chain. PEEK is opaque because of its semicrystalline nature at room temperature.

Refractive Index. The refractive index of F-PEEK was measured as one of the optical properties. Table 2 shows the wavelength-dependent refractive index data. The refractive index value of F-PEEK was sufficiently high: 1.646 at a typical wavelength of 589 nm, which is very high in comparison to the values reported so far for polymers in the optical field except for polymers containing heteroatoms in the skeleton.[11] The markedly high refractive index value of F-PEEK is probably attributable to the nature of the polynuclear aromatic main chain consisting of both the fluorene and naphthalene skeletons.

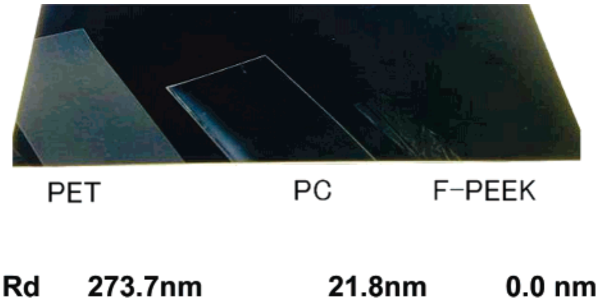


Figure 5. Birefringence of PET, PC, and F-PEEK obtained by the measurement with a polarized optical microscopy under the cross-Nicols at wavelength of 546 nm. The samples for the measurement were arranged to 200 μm thickness. PET, PC, and F-PEEK films had its retardation (Rd) of 273.7, 21.8, and 0 nm for the visible light (546 nm).

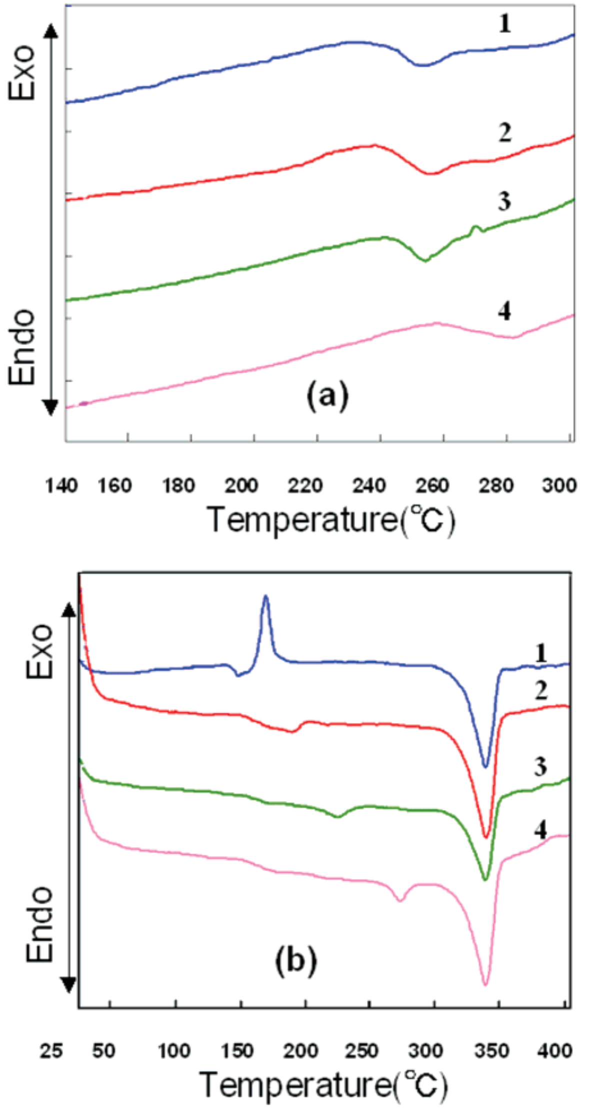


Figure 6. DSC traces of quenched films of F-PEEK (a) and PEEK (b) after annealing at different temperatures. Temperature from room temperature to 400 °C. 1: quenched film; 2: quenched film obtained after annealing at 200 °C for 1 h; 3: quenched film obtained after annealing at 250 °C for 1 h; 4: quenched film obtained after annealing at 300 °C for 1 h.

Birefringence. It can be seen from Figure 5 that the degree of birefringence of F-PEEK was lower than that of PC and much lower than that of PET. The degree of retardation (Rd) of visible light at 546 nm in F-PEEK was differed widely from that of PC and of PET. F-PEEK had zero retardation to visible light, but PC and PET showed retardations of 21.8 and 273.7 nm, respectively. The high birefringence of PC might be related to its linear main chain structure producing the optical anisotropy. The much lower birefringence of F-PEEK is possibly attributed to the *cardo* structure of the 9,9-diarylfluorene moiety in the main chain. The fluorene moiety and the two phenyl groups at the 9-posistion of the fluorene group occupy different planes and are crossed at the precise angle (Figure 1) that renders the structure most stable. Placing the aromatic rings on different planes might disturb their one-directional folding, and the optical anisotropy of F-PEEK could disappear.

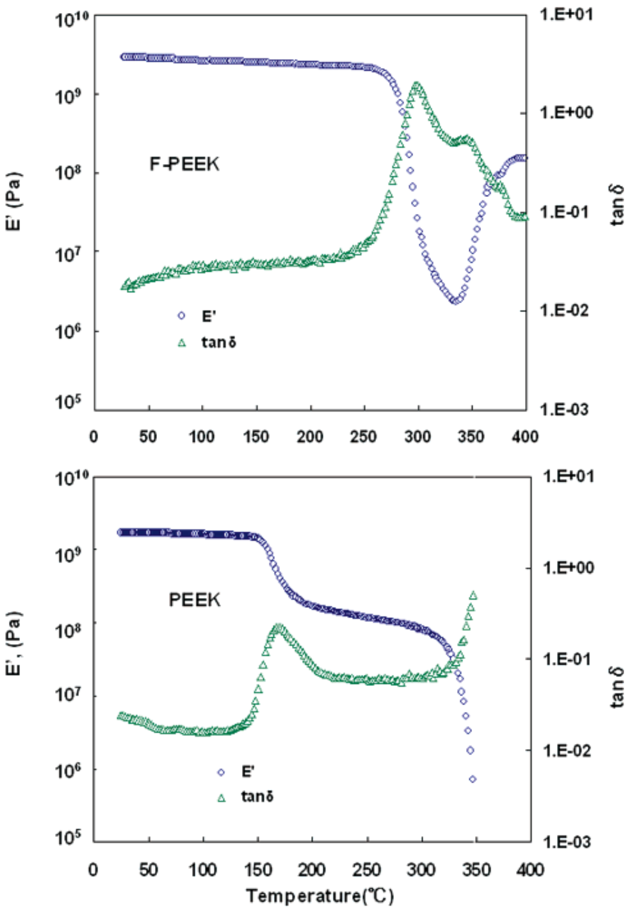


Figure 7. Viscoelastic properties of F-PEEK (top) and PEEK (bottom). Temperature from room temperature to 400 °C. The circle and triangle exhibit E' and tan δ, respectively.

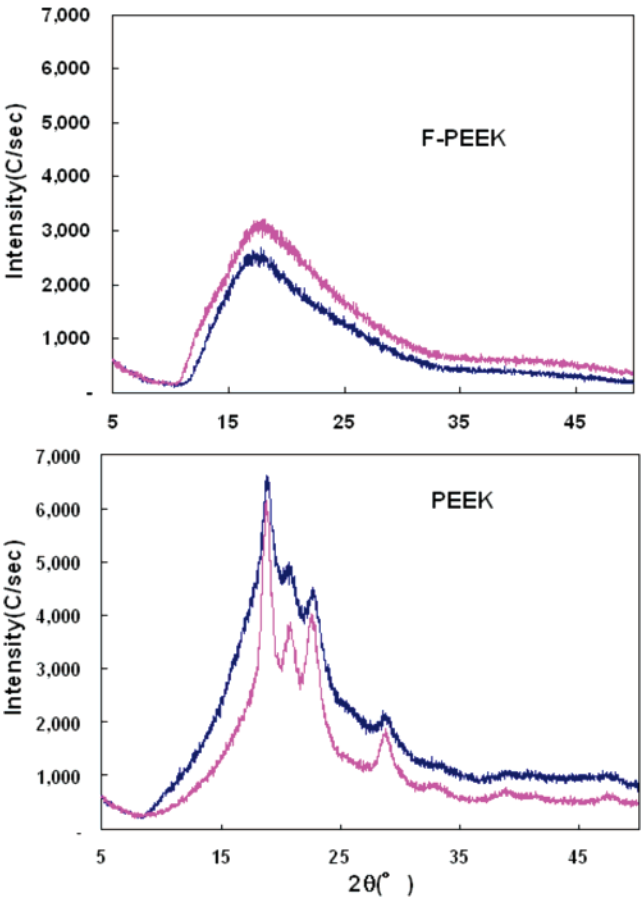


Figure 8. X-ray diffraction patterns of F-PEEK (top) and PEEK (bottom). The samples are thin films quenched and annealed at 250 °C for 30 min.

Thermal Properties. DSC traces of F-PEEK and PEEK films treated with and without annealing are shown in Figure 6. All F-PEEK samples annealed at different temperatures showed similar endothermal peaks around 250 °C. The signals can be regarded as glass transition temperature signals of the F-PEEK samples (T_g 280 °C). The measurement of the viscoelastic property of F-PEEK also suggested T_g of F-PEEK (299 °C), as discussed in the following part. The sample recovered after the DSC measurement kept its transparency of more than 80% at 600 nm. Meanwhile, PEEK showed T_g, T_c, and T_m at 147, 169, and 340 °C, respectively. The phase transition was confirmed during the annealing process of PEEK. By annealing PEEK at 200 °C (temperature higher than its crystallization temperature), PEEK was crystallized, while the relaxation due to the amorphous region disappeared: the DSC curve was almost flat at a temperature of around 147 °C, i.e., T_g of PEEK. It seems that PEEK was transferred to a transition state with higher energy to show a higher phase transition temperature by increasing the annealing temperature (Figure 6b, curves 2−4). In the case of F-PEEK, however, only a glass transition point was observed. This represents additional evidence of the amorphous nature of F-PEEK.

Viscoelastic Property. Figure 7 shows the viscoelastic property of F-PEEK and PEEK. Inspection of the curves and data suggested that the storage modulus was unchanged as 2.93×10^9 Pa until 280 °C. This is probably due to the extremely low molecular mobility of F-PEEK. The peak at 299 °C of the tan δ curve was assigned as T_g of F-PEEK, whereas the small peak around 350 °C was taken as the chain folding or the T_m of F-PEEK. F-PEEK kept its high storage modulus over 350 °C, possibly due to the steric hindrance of the fluorene group. In the case of PEEK, the storage modulus was 1.7 times lower than that of F-PEEK, and it largely decreased at 169 and 350 °C, where PEEK turned to the liquid state. The high heat-resistant property of F-PEEK might come from its rigid structure consisting of both fluorene- and naphthalene-based skeletons.

X-ray Diffraction Analysis. The wide-angle X-ray diffraction profiles of the samples quenched and annealed at 250 °C for 30 min are indicated in Figure 8. F-PEEK showed only an amorphous pattern for either quenched or annealed samples. PEEK samples displayed a crystalline pattern in both the quenched and annealed samples. The quenched sample had a crystallinity of 17%, while the annealed sample had a crystallinity of 29.7%. Because PEEK has a linear molecular structure, it is expected to display a higher crystallinity. The bulky and nonplanar molecular structures of the fluorene- and naphthalene-containing F-PEEK main chain seem to reduce crystallinity.

Conclusion

In the present study a novel poly(ether−ether−ketone) (F-PEEK) was designed and synthesized by combining 9,9-diarylfluorene and 1,5-bis(haloaroyl)-2,6-dimethylnaphthalene skeletons. The synthesis of F-PEEK was achieved by the polycondensation of 9,9-bis(3-methyl-4-hydroxyphenyl)fluorene (BHF) and 1,5-bis(4-fluorobenzoyl)-2,6-dimethylnaphthalene (DFA), in the presence of cesium carbonate as base in diphenyl sulfone as solvent via two-step heating. High molecular weight F-PEEK ($M_w > 270\,000$) was obtained quantitatively. F-PEEK was characterized by extraordinary properties such as high transparency, high refractive index, low birefringence, and high thermal stability in addition to high solubility, in comparison with PC, PET, and PEEK. The outstanding physical and mechanical properties of F-PEEK could be the result of the 9,9-diarylfluorene and 1,5-diaroyl-2,6-naphthalene moieties, suggesting the significance of the introduction of the nonplanar aromatic structures represented by the *cardo* structure in the main chain. F-PEEK can unambiguously be regarded as a promising advanced material that may be applied to various fields including optical material fields.

References and Notes

(1) Roeder, J.; Silva, H.; Nunes, S. P.; Pires, A. T. N. *Solid State Ionics* **2005**, *176*, 1411−1417.

(2) Abate, L.; Calanna, S.; Pollicino, A.; Recca, A. *Polym. Eng. Sci.* **1996**, *36*, 1782−1788.

(3) Rao, M. R.; Rao, V. L.; Radhakrishnan, T. S.; Ramachandran, S. *Polymer* **1992**, *33*, 2834−2839.

(4) Hoffmann, T.; Pospiech, D.; Haussler, L.; Komber, H.; Voigt, D.; Harnisch, C.; Kollann, C.; Ciesielski, M.; Doring, M.; Perez-Graterol, R.; Sandler, J.; Altstadr, V. *Macromol. Chem. Phys.* **2005**, *206*, 423−431.

(5) Watters, E. P. J.; Spedding, P. L.; Grimshaw, J. M.; Duffy, J. M.; Spedding, R. L. *Chem. Eng. J.* **2005**, *112*, 137−144.

(6) Ohno, M.; Takata, T.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 2647-−2655.

(7) Ohno, M.; Takata, T.; Endo, T. *React. Funct. Polym.* **1996**, *30*, 149-−156.

(8) Ohno, M.; Takata, T.; Endo, T. *Macromolecules* **1994**, *27*, 3447.

(9) Matsumura, S.; Kihara, N.; Takata, T. *High Perform. Polym.* **2001**, *13*, S293−S304.

(10) Matsumura, S.; Kihara, N.; Takata, T. *Macromolecules* **2001**, *34*, 2848−2853.

(11) Matsumura, S.; Kihara, N.; Takata, T. *J. Appl. Polym. Sci.* **2004**, *92*, 1869−1874.

(12) Matsumura, S.; Kihara, N.; Takata, T. *Kagaku Kogyo* **2001**, *75*, 494−500.

(13) Yao, K.; Koike, M.; Suzuki, Y.; Sakurai, K.; Indo, T.; Igarashi, K. US Patent 6,255,031, 2001.

(14) Sakurai, K.; Fuji, M. *Polym. J.* **2000**, *32*, 676−682.

(15) Inada, T.; Masunaga, H.; Kawasaki, S.; Yamada, M.; Kobori, K.; Sakurai, K. *Chem. Lett.* **2005**, *34*, 524−525.

(16) Okamura, H.; Mitsukura, K.; Shirai, M.; Fujiki, T.; Yamada, M.; Kawasaki, S. *J. Photopolym. Sci. Technol.* **2005,** *18*, 213−220.

(17) Okamura, H.; Harada, C.; Tsunooka, M.; Fujiki, T.; Kawasaki, S.; Yamada, M.; Shirai, M. *Kobunshi Ronbunshu* **2004**, *61*, 75−81.

(18) Okamura, H.; Sakai, K.; Tsunooka, M.; Shirai, M.; Fujiki, T.; Kawasaki, S.; Yamada, M. *J. Photopolym. Sci. Technol.* **2003**, *16*, 87−90.

(19) Okamura, H.; Watanabe, Y.; Tsunooka, M.; Shirai, M.; Fujiki, T.; Kawasaki, S.; Yamada, M. *J. Photopolym. Sci. Technol.* **2002**, *15*, 145−152.

(20) Tokumitsu, K.; Tanaka, A.; Kobori, K.; Kozono, Y.; Yamada, M.; Nitta, K.-H. *J. Polym. Sci., Part B: Polym. Phys.* **2005**, *43*, 2259−2268.

(21) Kawasaki, S.; Yamada, M.; Kobori, K.; Yamada, M.; Kakumoto, T.: Tarutani, A.; Takata, T. *Polym. J.* **2007**, *39*, in press.

MA070589N