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Synthesis of a Novel Naphthalene-Based Poly(arylene ether ketone) with High Solubility and Thermal Stability

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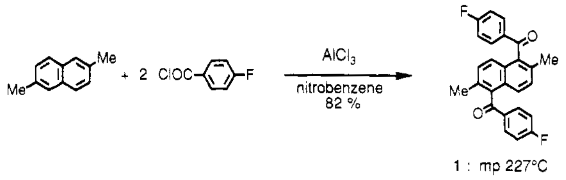
Introduction. Poly(arylene ether ketone)s (PEKs) are known as one of the high-performance engineering thermoplastics having high glass transition temperature (T_g, higher than 150 °C) and chemical stability. Several PEKs such as poly(arylene ether ether ketone)[1] are commercially available and have been utilized as coatings, adhesives, composites, and molded components. Hergenrother *et al.*[2] have reported PEKs with 2,6-naphthylene moieties whose T_gs were higher than those of PEKs containing phenylene moieties. Semicrystalline PEKs are also characterized by high molding temperature and low solubility in common organic solvents in contrast to the excellent properties mentioned above. To enhance the solubility, Ritter *et al.*[3] have synthesized 1,5-naphthylene-based PEKs with long alkoxy side chains, which show good solubility but low thermal stability. Furthermore, Maier *et al.*[4] have reported indan-based PEKs having good solubility and high thermal stability (T_g 167–213 °C). Meanwhile, it has been reported that both 1,5-naphthylene unit and methyl groups on the aromatic rings of a polyimide backbone enhance the T_gs.[5] Introduction of methyl groups onto the polymer main chain can increase the solubility of the polymers, especially in the case of all aromatic polymers. In this paper, we describe the synthesis of a novel dimethylnaphthalene-based polymer having both high thermal stability and solubility.

Results and Discussion. Friedel–Crafts acylation of 2,6-dimethylnaphthalene with 4-fluorobenzoyl chloride was carried out at 80 °C in nitrobenzene in the presence of aluminum chloride in nitrobenzene to give the difluoroarene formulated as 1 in 82% yield (Scheme 1).[6] Occurrence of the regioselective dibenzoylation at sterically hindered 1- and 5-positions of the naphthalene ring was confirmed by the detailed ^{1}H-NMR study (500 MHz).

Polycondensation of 1 with Bisphenol A in toluene/*N*-methyl-2-pyrrolidone (NMP) was carried out at 180 °C for 3 h in the presence of a slight excess of potassium carbonate as a condensation reagent,[7] after the reaction temperature was maintained at 140 °C for 1 h to remove water by azeotropic distillation with toluene. Polymer obtained quantitatively by precipitation from methanol was determined to be poly(arylene ether ketone) **2**[8] by spectral analyses (Scheme 2).

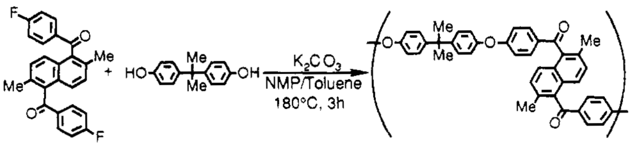
Figure 1 shows the ^{1}H-NMR spectra of **2** and its model compound **3** which was prepared by the reaction of **1** with 4-isopropylphenol under similar conditions. All signals corresponding to the unit structure of **2** were clearly observed. Namely, two singlets attributable to g and h methyl protons appeared in equal intensity at 1.7 and 2.3 ppm, respectively, and five doublets based on the aromatic protons (a–f) were observed at 6.8–7.9 ppm. This spectrum was in good agreement with that of the model compound **3** especially in the aromatic region, suggesting the proposed polymer structure of **2**. Polymer **2** showed exceptionally high solubility: **2** was readily soluble in not only dimethyl sulfoxide (DMSO) but also chloroform and tetrahydrofuran (THF) at room temperature.

Scheme 1



1 : mp 227°C

Scheme 2



1

2 ; quant.

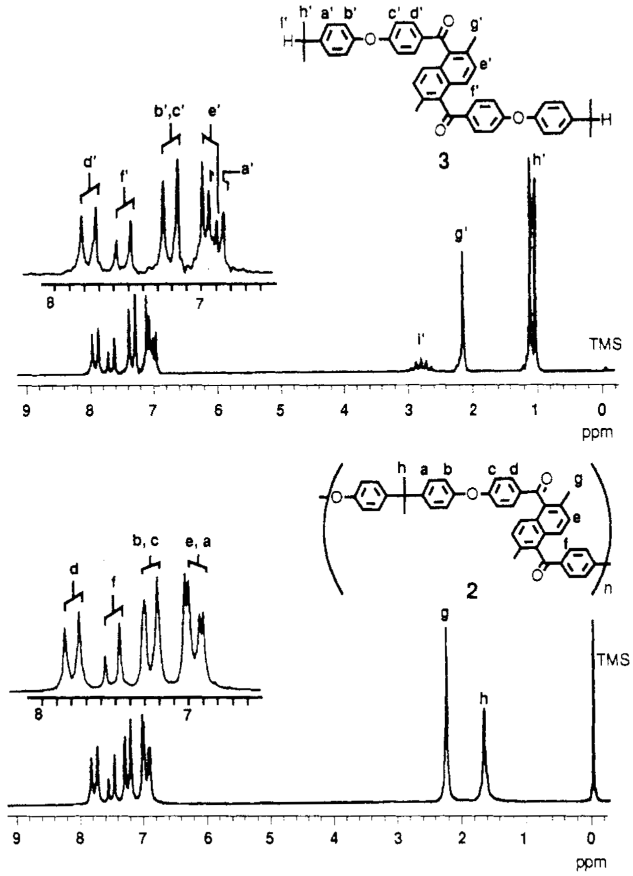


Figure 1. ^{1}H-NMR spectra of **2** (bottom) and its model compound **3** (top) in $CDCl_3$ at room temperature.

The gel permeation chromatogram of **2** (eluent: THF) involved a unimodal peak with $\bar{M}_n$ 34 900 ($\bar{M}_w/\bar{M}_n$ 1.96). As the reaction time was prolonged, both $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ increased and the polymer obtained after 24 h of polymerization had a $\bar{M}_n$ of more than 100 000 (Table 1). DMSO employed instead of NMP as the reaction solvent afforded a similar result, whereas by polymerization in sulfolane polymer **2** was obtained with a higher molecular weight than that of the polymer obtained in NMP (Table 1).

In thermal analysis, polymer **2** exhibited no melting endotherms but sufficiently high T_g (222 °C, heating rate of 20 °C/min under a nitrogen atomosphere) and 5%

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Table 1. Polycondensation of 1 with Bisphenol A[a]

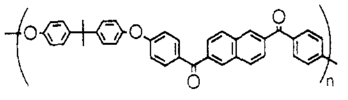
time (h)	yield (%)[b]	solvent	$\bar{M}_n/10^4$ [c]	$\bar{M}_w/\bar{M}_n$[c]
4	quant	NMP	3.49	1.96
16	quant	NMP	6.22	1.93
24	quant	NMP	10.2	2.47
4	quant	DMSO	3.28	1.80
4	quant	sulfolane	4.80	1.81

[a] The polycondensation was carried out with 3 mmol of 1, 3 mmol of Bisphenol A and K_2CO_3 (8 mmol) in toluene (15 mL)/NMP (6 mL). [b] Methanol-insoluble part. [c] Estimated by GPC (eluent: THF) based on PSt standards.

weight loss temperature (T_{d_5} 457 °C, heating rate of 20 °C/min in air), revealing its high thermal stability.

In accordance with good solubility and high molecular weight as mentioned above, a self-standing, transparent, flexible, and amorphous film could be prepared by casting from a THF or chloroform solution of 2.

As described above, we could prepare novel poly(arylene ether ketone) 2 possessing both high solubility and thermal stability by using 1,5-bis(4-fluorobenzoyl)-2,6-dimethylnaphthalene (1) as the difluoroarene moiety. Poly(arylene ether ketone) 4 which was prepared independently from 2,6-bis(4-fluorobenzoyl)naphthalene and Bisphenol A for comparison showed a lower T_g (185 °C) than 2 and was insoluble in ordinary organic solvents such as DMSO.[2]



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The pronounced good properties of 2 originated from the 2,6-dimethylnaphthylene skeleton. The high solubility of 2 compared with that of 4 might come from the unique structure of 2 (or 1) in which two benzoyl groups are not coplanar with the naphthalene ring probably due to the steric repulsion of the neighboring two methyl groups situated at the 2- and 6-positions and two hydrogens at the peri position, as suggested by the X-ray crystal structural analysis of 1.[9] Thus, this work presents a high-performance PEK which has both high solubility and thermal stability, using the novel naphthalene-based difluoroarene monomer.

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References and Notes

(1) Atwood, T. E.; Barr, D. A.; King, T. A.; Newton, B.; Rose, J. B. *Polymer* **1977**, *18*, 359.

(2) Hergenrother, P. M.; Jensen, B. J.; Havens, S. J. *Polymer* **1988**, *29*, 358.

(3) Ritter, H.; Thorwirth, R. *Makromol. Chem.* **1993**, *194*, 1469.

(4) Maier, G.; Yang, D.; Nuyken, O. *Makromol. Chem.* **1993**, *194*, 1901.

(5) Mita, I. In *Koseino Hokozokukei Kobunshi Zairyo*; Maruzen, Ed.; The Society of Polymer Science, Japan: Tokyo, Japan, 1990; Chapter 2, pp 22 and 23.

(6) Anhydrous aluminum chloride (1.920 g, 14.4 mmol) was added in small portions to a cold (0–5 °C) stirred solution of a mixture of 2,6-dimethylnaphthalene (937.4 g, 6.00 mmol) and 4-fluorobenzoyl chloride (2.283 g, 14.4 mmol) in nitrobenzene (or chloroform, 10 mL) during a period of 15 min. The reaction mixture was stirred at this temperature for 1 h. The reaction temperature was raised up to 80 °C (or chloroform reflux) and then stirred for an additional 3 h. The resulting mixture was poured into cold, hydrochloric acid and stirred for 1 h. Methanol was poured into the residue obtained by decantation to precipitate a white solid. The solid was recrystallized twice from acetone to afford 1,5-bis(4-fluorobenzoyl)-2,6-dimethylnaphthalene (1) as white crystals (82% (in nitrobenzene), 75% (in $CHCl_3$) yield). 1: mp 226–227 °C; IR (KBr) 1595, 1503 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.27 (s, 6H), 7.11 (dd, 2H, J = 8.7, 8.7 Hz), 7.27 (d, 2H, J = 9.0 Hz), 7.48 (d, 2H, J = 9.0 Hz), 7.84 (dd, 2H, J = 5.4, 8.7 Hz); ^{13}C-NMR ($CDCl_3$) δ 19.6, 116.2 (d, J = 20.7 Hz), 125.9, 128.8, 129.5, 131.9, 132.5 (d, J = 9.6 Hz), 133.9 (d, J = 2.8 Hz), 135.9. Elem. Anal. Calcd for $C_{26}H_{18}O_2F_2$: C, 78.0; H, 4.5. Found: C, 78.2; H, 4.4.

(7) The polycondensation was carried out with 3 mmol of 1 (1.20 g), 3 mmol of Bisphenol A (685 mg), and K_2CO_3 (1.11 g) in toluene (15 mL)/NMP (6 mL). The polymerization mixture obtained was quenched by addition of trifluoroacetic acid, and polymer 2 was obtained by precipitation with methanol (100 mL).

(8) 2: IR (KBr) 1244, 1667 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.69 (s, 6H), 2.27 (s, 6H), 6.94 (d, 2H, J = 5.8 Hz), 6.97 (d, 2H, J = 8.7 Hz), 7.24 (d, 4H, J = 4.4, 5.8 Hz), 7.50 (d, 2H, J = 8.7 Hz), 7.75 (d, 2H, J = 4.4 Hz); ^{13}C-NMR ($CDCl_3$) δ 19.4, 30.9, 42.3, 117.1, 119.9, 125.7, 128.3, 128.7, 129.2, 131.5, 131.8, 132.0, 136.1, 147.0, 152.8, 162.9, 198.3. Elem. Anal. Calcd for $C_{39}H_{32}O_4$: C, 83.0; H, 5.7. Found: C, 82.8; H, 5.8.

(9) Crystal data of 1: $C_{26}H_{18}O_2F_2$, M = 400.4, $Pca21$, a = 12.9244 (3) Å, b = 7.1524 (3) Å, c = 21.5682 (3) Å, $\alpha = \beta = \gamma$ = 90°, V = 1993 Å^3, Z = 4, R = 0.044.