Naphthalene-based poly(aryl ether)s. II. Synthesis and characterization of poly(ether ketone)s containing two 1,4-naphthylene moieties in the repeat unit

Zhi Yuan Wang and Peter W. Broughton

Abstract: Two new monomers, 4-chloro-1-(4′-fluoro-1-naphthoyl)naphthalene and 1,4-bis(4′-fluoro-1′-naphthoyl)benzene, have been synthesized and polymerized with four different bisphenols to give two series of the naphthalene-based poly(ether ketone)s that are analogous to commercial PEEK and PEEKK. The effect of the introduction of one or two 1,4-naphthylene moieties, in the backbone of the repeat unit, on the glass transition temperatures has been studied. The glass transition temperatures usually increased by 20–45°C upon replacing one 1,4-phenylene with one 1,4-naphthylene moiety. All new poly(ether ketone)s prepared in tetramethylene sulfone were amorphous, with the glass transition temperatures in a range of 212–273°C. The polymer produced from 1,4-bis(4′-fluoro-1′-naphthoyl)benzene and 1,4-hydroquinone in phenyl sulfone as a solvent at 300°C showed semicrystalline properties with a melting temperature of 310°C.

Key words: naphthalene, poly(ether ketone)s, synthesis, characterization, glass transition temperature.

Résumé : On a synthétisé deux nouveaux monomères, le 4-chloro-1-(4′-fluoro-1′-naphtoyl)naphtalène et le 1,4-bis(4′-fluoro-1′-naphtoyl)benzène, et on les a polymérisés avec quatre différents biphénols pour obtenir une série de poly(éther cétone), contenant du naphtalène, qui sont analogues aux polymères commerciaux PEEK et PEEKK. On a étudié l'influence de l'insertion d'une ou deux unités, 1,4-naphtylène, dans le squelette du monomère, sur les températures de transition du verre. Les températures de transition du verre augmentent habituellement par 20–45°C lorsqu'on remplace une unité 1,4-phénylène par une unité 1,4-naphtylène. Tous les nouveaux poly(éther cétone) préparés dans le tétraméthylène sulfone sont amorphes et les températures de transition du verre sont de l'ordre de 212–273°C. Le polymère obtenu par polymérisation du 1,4-bis(4′-fluoro-1′-naphtoyl)benzène avec la 1,4-hydroquinone dans le phényl sulfone comme solvant montre à 300°C des propriétés semi-cristallines avec une température de fusion de 310°C.

Mots clés : naphtalène, poly (éther cétone), synthèse, caractérisation, température de transition du verre.

[Traduit par la rédaction]

Introduction

Aromatic poly(ether ketone)s (1) make up one of the major polymer families that are known for their superior performance characteristics in an unsurpassed number of application areas. Poly(ether ketone)s **1a** (2, 3) and **4a** (3) (Fig. 1) are typical examples, commercially available under the trade names of Victrex PEEK and Hostatec PEEKK, respectively. Key properties of these two poly(ether ketone)s, such as excellent thermal and oxidative stability, superior chemical resistance, high mechanical strength and stiffness, and excellent wear and abrasion resistance, allow them to be used as bearings, seals, wear rings, wire and cable coatings, composite matrices, and compressor parts. It has long been recognized that the fundamental basis for their performance resides in the phenylene–ether–ketone linkages that are present in their polymeric structures. The semicrystalline nature of **1a** and **4a**, as characterized by a melting point (T_m) of 344°C for **1a** and 358°C for **4a** (4), can be attributed to the regular phenylene–ether–ketone structure in their backbones. However, due to the same structural features, amorphous **1a** and **4a** exhibit relatively low glass transition temperatures (T_g) of 143°C and 154°C, respectively.

Earlier work of ours showed that the replacement of one 1,4-phenylene with one 1,4-naphthylene moiety in the repeat unit of poly(ether ketone) **1a** significantly reduced the crystallinity and increased the T_g of the resulting polymer **2a** to 188°C (up by 45°C) (5). Insertion of the 1,4-naphthylene moiety is equivalent to the addition of a benzo moiety perpendicular to the 1,4-phenylene unit in the main chain of poly(ether ketone)s. Thus, incorporation of two 1,4-naphthylene units into poly(ether ketone)s seemed worthwhile as it could further increase the T_g and reduce their crystallinity. In this paper, we report the synthesis and characterization of two series of poly(ether ketone)s (**3** and **5**) containing two naphthalene

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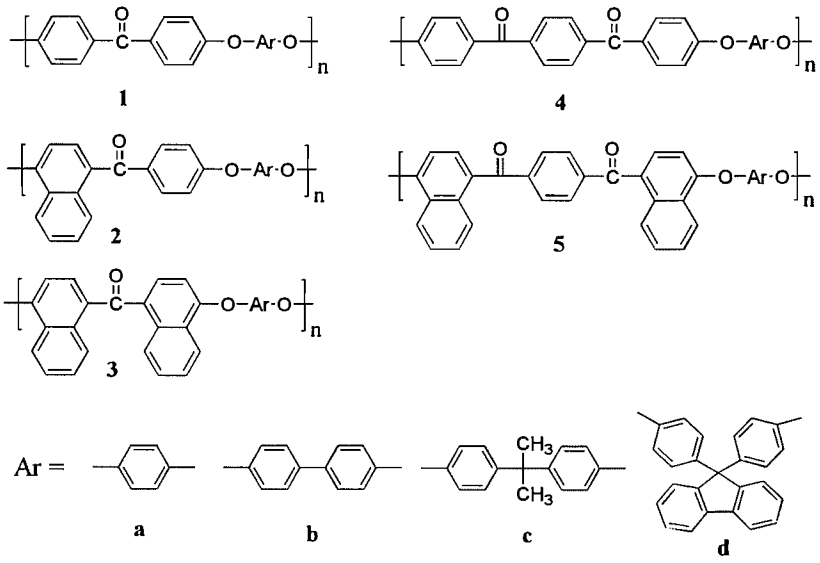
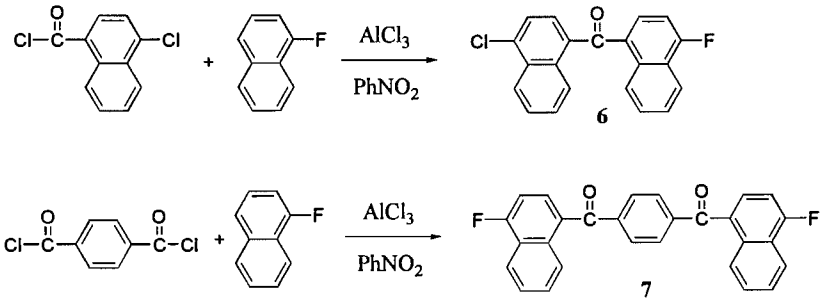
Fig. 1. Phenylene- and naphthylene-containing poly(ether ketone)s **1**–**5**.



Scheme 1. Synthesis of naphthalene-based monomers **6** and **7**.



rings in the repeat unit (Fig. 1). This study is part of an ongoing effort by our group to investigate structure–property relationships of poly(ether ketone)s and to design and identify potential new high-performance thermoplastics.

Results and discussion

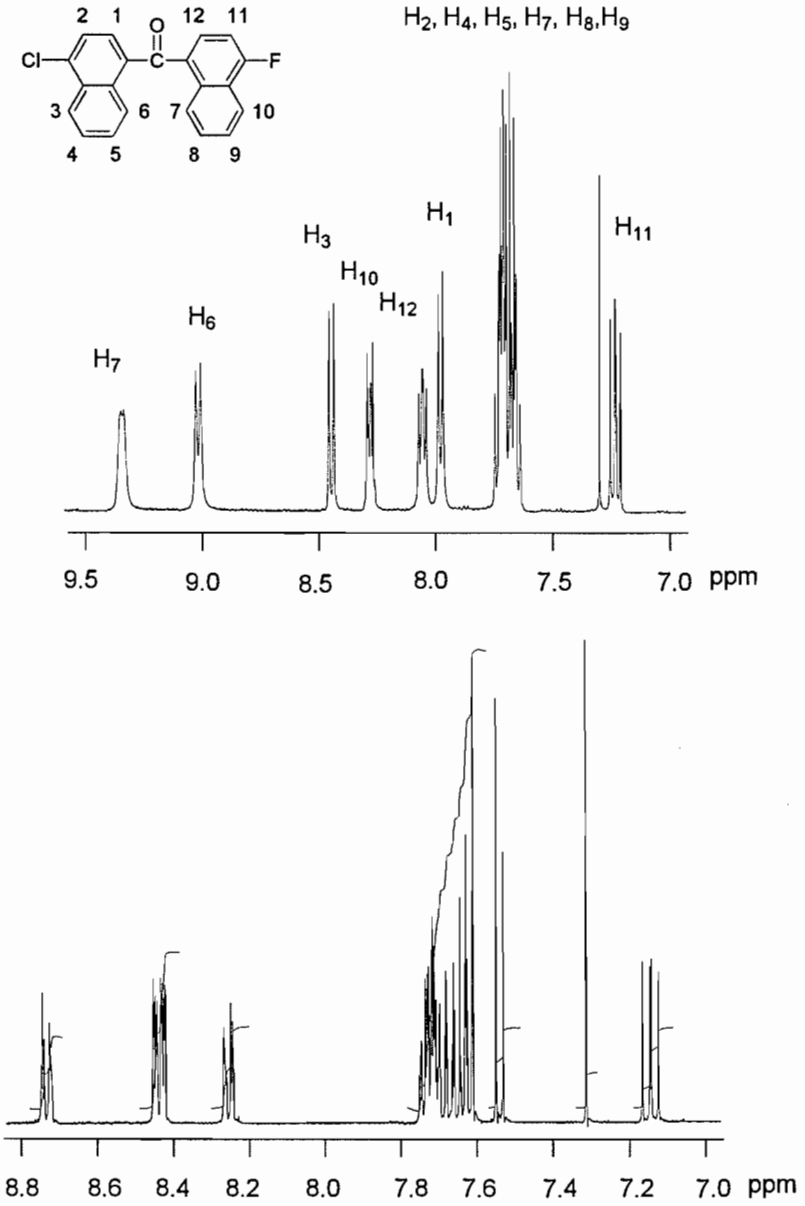
Monomer synthesis

Incorporation of the 1,4-naphthylene unit in poly(ether ketone)s was accomplished through the syntheses and polycondensations of two new dihalide monomers, 4-chloro-1-(4′-fluoro-1-naphthoyl)naphthalene (**6**) and 1,4-bis(4′-fluoro-1-naphthoyl)benzene (**7**). The Friedel–Crafts acylation route was used, based on 1-fluoronaphthalene, 4-chloro-1-naphthaloyl chloride, and terephthaloyl chloride as starting materials (Scheme 1). 4-Chloro-1-naphthoic acid was obtained by hypochlorite oxidation of 4-chloro-1-acetonaphthone, which was prepared by acylation of 1-chloronaphthalene with acetyl chloride (6). The transformation of 4-chloro-1-naphthoic acid to the acid chloride was done using an excess of thionyl chloride in high yield. The subsequent Friedel–Crafts reaction was carried out at 70–80°C with a 3:1 molar ratio of 1-fluoronaphthalene to the acid chloride in nitrobenzene. Monomer **6** was obtained in good yield as yellow crystals with a melting point of 111–112°C after purification, twice by vacuum distillation, followed by recrystallization from xylenes. It was soluble in the solvents suitable for polymerization such as *N*-methyl-2-pyrrolidinone (NMP), *N*,*N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), and tetramethylene sulfone ($TMSO_2$).

Monomer **6** was fully characterized by spectroscopic means. The presence of two magnetically nonequivalent 1,4-naphthylene moieties and the long-range F–H couplings made its ^{1}H NMR spectrum very complicated (bottom of Fig. 2). However, the use of the $Eu(fod)_3$ lanthanide shift reagent, coupled with COSY and HETCOR experiments, allowed us to obtain the well-resolved ^{1}H NMR spectrum of **6** and a complete assignment (top of Fig. 2). The ^{19}F NMR spectrum displayed only one peak at -114.15 ppm relative to CCl_3F. The IR spectrum of **6** showed a peak at 1645 cm^{-1}, attributed to the conjugated ketone. MS gave the parent molecular ion at *m*/*z* 334 and the base peak at *m*/*z* 173, corresponding to the loss of the fluoronaphthoyl radical. The rest of the fragmentation patterns were indicative of the structure. Moreover, HRMS indicated the correct molecular formula.

The synthesis of the monomer **7** was achieved in good yield by the Friedel–Crafts acylation of 1-fluoronaphthalene using a 2.6:1 molar ratio of aluminum chloride to terephthaloyl dichloride in nitrobenzene (Scheme 1). Recrystallization three times from DMF afforded **7** in high purity as a yellow crystal-

Fig. 2. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of monomer **6** (2.5 mg); top: containing 11 mg of $Eu(fod)_3$; bottom: without $Eu(fod)_3$.



line solid with a melting point of 230–231°C. Its structure was consistent with the ^{1}H and ^{13}C NMR data supported by COSY and HETCOR experiments. The ^{19}F NMR spectrum of **7** displayed a peak at −114.81 ppm relative to CCl_3F. The IR spectrum showed a strong peak at 1651 cm^{-1}, indicating the conjugated carbonyl moiety. MS gave the parent molecular ion at *m/z* 422, as expected, and the base peak at *m/z* 173 corresponding to the fragment ion due to the loss of fluoronaphthoyl radical. HRMS indicated the correct molecular formula.

Polymer synthesis

The following common solvents for nucleophilic substitution polycondensations were tested in the syntheses of polymers **3** and **5**: NMP, DMAc, and $TMSO_2$. In NMP, it was found that the cleavage of the ether linkage of the resulting poly(ether ketone)s occurred at elevated temperatures as reported before (7). DMAc was also not a suitable solvent, since the resulting polymers **3** and **5** exhibited very limited solubility. Polymerizations were then best carried out at 210°C in $TMSO_2$ with chlorobenzene as an azeotroping agent using a stoichiometric mixture of a dihalide and a bisphenol in the presence of potassium carbonate (2 mol-equiv.). The water formed during the reaction was removed as an azeotrope with chlorobenzene at 140°C over a period of 1–2 h. The polymerization temperature was then gradually raised to 210°C. The polymerization was stopped when the molecular weight, as analyzed by gel permeation chromatography (GPC), began to decrease. The resulting polymers were coagulated in an excess of methanol, followed by reverse precipitation to remove any remaining oligomers.

Under these reaction conditions, polymers **3** and **5** were obtained as off-white to yellow fibrous solids in moderate to high molecular weights. However, polymers **3a, b** and **5a, b** still exhibited low solubility in $TMSO_2$ and precipitated out of

Table 1. Characterizations of polymers **3** and **5**.

Polymer	M_w ($\times 10^{-4}$)	M_n ($\times 10^{-4}$)	M_w/M_n	η_{inh}[a](dL/g)	T_d[b](N_2)	T_d[b](air)
3a	N/A	N/A	N/A	0.31[c]	510	524
3b	N/A	N/A	N/A	0.31[c]	488	466
3c	5.71	2.13	1.58	0.24	497	478
3d	3.80	2.13	1.78	0.23	525	453
5a	N/A	N/A	N/A	0.33[c]	493	489
5a[d]	N/A	N/A	N/A	0.23[c]	504	474
5b	N/A	N/A	N/A	0.34[c]	480	430
5c	5.71	2.74	2.08	0.34	492	436
5d	8.32	4.12	2.02	0.66	526	464

[a]In 0.5% chloroform at 25°C.
[b]Onset temperature for 5% weight loss by TGA.
[c]In 0.5% NMC at 25°C.
[d]Polymerized in phenyl sulfone; N/A = not available.

solution prematurely during polymerization. Although being soluble in high-boiling 1-cyclohexyl-2-pyrrolidinone (bp 280°C) and *N*-methylcaprolactam (NMC, bp 260°C), polymers **3a, b** and **5a, b** with higher molecular weights could not be obtained in these two solvents.

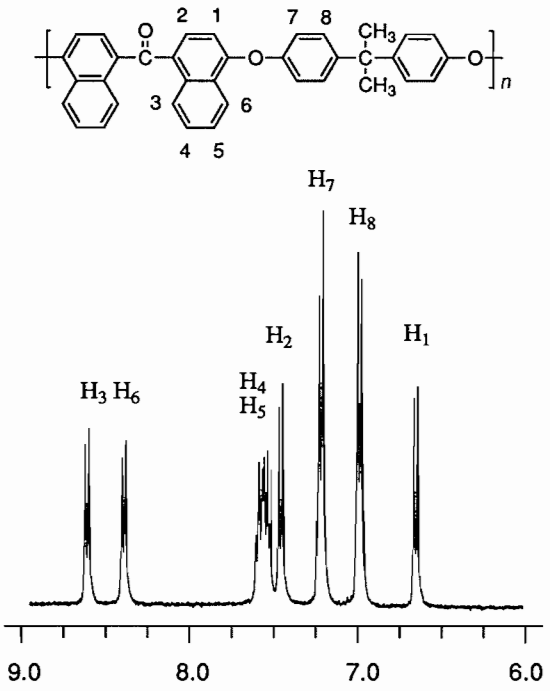
Phenyl sulfone (bp 379°C) is frequently used as a high-boiling solvent for the preparation of semicrystalline poly(aryl ether)s such as PEEK (2). Thus, the polymerization of **7** and 1,4-hydroquinone was performed in phenyl sulfone at 300°C. Although having a molecular weight similar to the sample prepared in $TMSO_2$, polymer **5a** produced in phenyl sulfone appeared to be semicrystalline and showed a T_m of 310°C by differential scanning calorimetry (DSC).

Polymer characterization

Polymers **3c, d** and **5c, d** containing the flexible isopropylidene and bulky spiro fluorene groups showed good solubility in chlorinated hydrocarbons, DMAc, and NMP. Polymers **3a, b** and **5a, b**, on the other hand, displayed much more solvent resistance than the others. Comparing three polymers **1a**, **2a**, and **3a** derived from 1,4-hydroquinone, PEEK (**1a**) is the most solvent resistant and polymer **2a** is the least solvent resistant. The former is only soluble in concentrated sulfuric acid at room temperature, while the latter is readily soluble in chloroform, 1,1,2,2-tetrachloroethane (TCE), DMAc, and NMP. However, the structurally related **3a**, having two naphthalene rings in the repeat unit, displayed much more solvent resistance than **2a**, being only soluble in NMP and *N*-methylcaprolactam (NMC). Thus, the good solubility of **2a** is attributed mainly to its microstructure, consisting of a random distribution of the head-to-tail, head-to-head, and tail-to-tail diads (5). A similar trend in solubility has been found for polymers **1b**, **2b**, and **3b**. Comparing polymers **4a,b** with polymers **5a,b**, the former two semicrystalline poly(ether ketone)s are insoluble in common organic solvents, and the latter two naphthalene-based analogues are soluble in NMP and NMC at ambient temperatures and can also be dissolved in hot TCE.

Polymers **3** gave much simpler NMR spectra than the spectrum of monomer **6**, due to the fact that two naphthylene units in the repeat unit of **3** are magnetically equivalent without the fluorine splitting. For example, the ^1H NMR spectrum of the aromatic region of polymer **3c** (Fig. 3) is simple and well

Fig. 3. ^1H NMR (400 MHz, $CDCl_3$) spectrum of the aromatic region of polymer **3c**.



resolved, yet still shows the characteristic pattern of the 1,4-naphthylene moiety. The methyl groups of the BPA unit in polymer **3c** appears as a singlet at 1.65 ppm but is not shown in Fig. 3. The peak assignments were supported by COSY and HETCOR experiments. The ^{13}C NMR spectrum of **3c** showed 17 distinguishable peaks for each of the magnetically non-equivalent carbon atoms. IR spectra indicated the carbonyl groups for polymers **3** and **5** in the region of 1648–1658 cm^{-1} and the ether linkages in the region of 1238–1243 cm^{-1}.

Polymers **3c** and **3d** had the same number-average molecular weight of 21 300, relative to polystyrene determined by GPC, and similar inherent viscosities of about 0.23 dL/g in chloroform (Table 1). In comparisons with **3c** and **3d**, polymers **5c** and **5d** had higher molecular weights (M_n = 27 400 and 41 200 for **5c** and **5d**, respectively) and higher inherent

Table 2. Comparison of T_g values of polymers **1**–**3**.

Polymer	T_g(°C) **1**[a]	T_g(°C) **2**[b]	T_g(°C) **3**	ΔT_g(°C) (**2** – **1**)	ΔT_g(°C) (**3** – **2**)	ΔT_g(°C) (**3** – **1**)
a	143	188	232	45	44	89
b	170	210	235	40	25	65
c	155	189	212	34	23	57
d	252	272	273	20	1	21

[a]Taken from ref. 4.
[b]Taken from ref. 5.

Table 3. Comparison of T_g values of polymers **4** and **5**.

Polymer	T_g(°C) **4**	T_g(°C) **5**	ΔT_g(°C) (**5** – **4**)
a	154[a]	217	63
b	168[b]	230	62
c	165[b]	204	39
d	243[b]	265	22

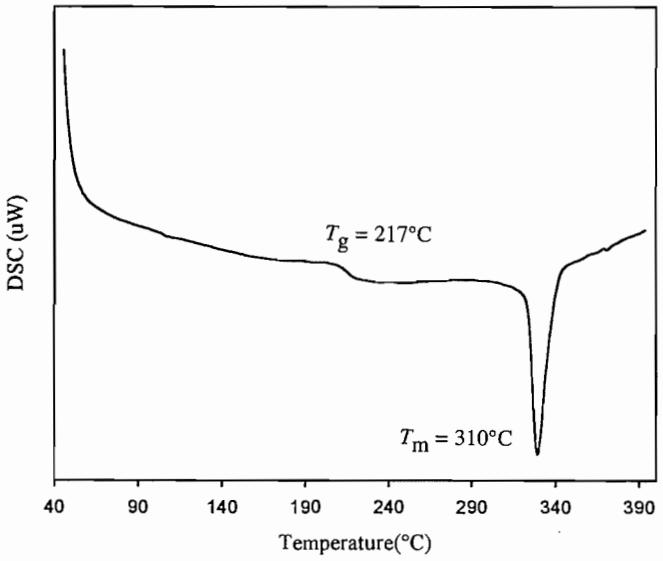
[a]Taken from ref. 3.
[b]Taken from ref. 4.

viscosities (0.34 and 0.66 dL/g). Less soluble polymers **3a, b** and **5a, b** had moderate molecular weights, as indicated by their inherent viscosities, above 0.30 dL/g in NMC (Table 1). Tough, flexible films were successfully prepared for polymers **3c, d** and **5c, d** but not for polymers **3a, b** and **5a, b**. Overall, polymers **3** were obtained in relatively lower molecular weights than polymers **5** under the same polymerization conditions.

The naphthalene-based poly(ether ketone)s **3** and **5** had high thermal and thermooxidative stabilities, comparable to the phenylene analogues **1** and **4**. The onset temperatures for 5% weight loss, as assessed by TGA, occurred above 480°C in nitrogen and 430°C in air (Table 1).

All polymers **3** and **5** produced in $TMSO_2$ showed no crystalline behavior as assessed by DSC. The T_g values for polymers **3** ranged from 212 to 273°C depending on the units derived from bisphenol monomers (Table 2). As expected, polymer **3c** had the lowest T_g (212°C), due to the presence of a flexible isopropylidene group, and polymer **3d** containing a bulky cardo group had the highest T_g of 273°C. By comparing with the T_g values of polymers **1** and **2**, the effect on the T_g of the insertion of the 1,4-naphthylene moiety in the backbone of the repeat unit can be seen clearly. On the basis of semicrystalline PEEK (**1a**), the T_g increases by 45°C upon the insertion of one naphthalene ring as in the case of **2a** (188°C) and further increases to 232°C (up by another 44°C) for polymer **3a** having two naphthalene rings in the repeat unit. Going from **1b** (8) and **1c** (1*a*, 9) to **2b** (10) and **2c** (5) the T_g values increase 35–40°C but only about 25°C from **2b** and **2c** to **3b** and **3c**. Similarly, there was a moderate increase of about 20°C in T_g from **1d** (9) to **2d** (5), but almost no difference in T_g between polymers **2d** and **3d**. For the diketone-containing polymers (**4** and **5**), the increase in T_g upon replacing 1,4-phenylene with 1,4-naphthylene in the repeat unit was also observed (Table 3). Polymers **5a** and **5b** had T_g values of 217 and 230°C, respectively, over 60°C higher than those of the phenylene analogues **4a** (3) (154°C) and **4b** (11) (168°C). A moderate increase (about 20°C and 40°C) was observed for the poly(ether ketone)s derived from 4,4′-isopropylidenediphenol and 9,9-bis(4-hydroxyphenyl)fluorene (**5c** and **5d**), in comparison with their analogues **4c** (1*a*) and **4d** (9).

Fig. 4. DSC trace of the polymer **5a** prepared in phenyl sulfone at 300°C.



Although amorphous when produced in $TMSO_2$, polymer **5a** appeared to be semicrystalline when it was prepared in phenyl sulfone at 300°C. The DSC trace showed a T_g of 217°C and a T_m of 310°C (Fig. 4). In comparison with its phenylene analogue **4a**, with a T_g of 154°C and a T_m of 358°C, the polymer **5a** prepared in phenyl sulfone had a much higher T_g and a slightly lower T_m. Accordingly, the semicrystalline **5a** has a higher T_g/T_m ratio (0.84) than that (0.68) of commercial PEEKK (**4a**), which is desirable when considering the melt-processing temperatures and the final-use temperatures of the polymer.

Thermomechanical measurements were performed on thin strips of flexible, tough films cast from chloroform solutions using a thermomechanical analyzer in the tensile stress–strain mode. Young's moduli of three polymers **3d**, **5c**, and **5d** were 1.20, 3.44, and 2.84 GPa, respectively, at 25°C. These values are comparable to those of the phenylene-based poly(ether ketone)s, indicative of the characteristics of high-performance thermoplastics.

Conclusion

Two series of the naphthalene-based poly(ether ketone)s analogous to commercial PEEK and PEEKK were prepared. It has been found that the increase in T_g upon replacing the 1,4-phenylene with the 1,4-naphthylene moieties in the repeat unit is much greater for the semicrystalline phenylene poly(ether ketone)s than for the amorphous analogues derived from 1,4-hydroquinone and 4,4-biphenol. Semicrystalline poly(ether ketone) **5a** shows potential as a new high-performance thermoplastic, owing to its high T_g and high T_g/T_m ratio.

Experimental section

General

Melting points were taken on a Fisher–Johns apparatus and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on either a Varian Gemini-200 or a Bruker-400 instrument using tetramethylsilane as the internal solvent. The ^{19}F NMR spectra were recorded on a Varian XL-300 using CCl_3F as a reference. Infrared measurements were performed on a Perkin–Elmer Series 1600 FTIR instrument. Molecular weights were determined on a Perkin–Elmer LC-250 GPC instrument relative to polystyrene standards using chloroform as an eluent at a flow rate of 1.0 mL/min; a UV detector was set at 254 nm wavelength. Inherent viscosities were measured in a 0.5 g/dL chloroform solution (or in *N*-methylcaprolactam where indicated) at 25°C using a Ubbelohde dilution viscometer. The glass transition temperatures were determined by differential scanning calorimetry (DSC) on a Seiko DSC 220 at a heating rate of 10°C/min under nitrogen (50 mL/min) and taken as the midpoint of the change in slope of the base line. Thermogravimetric analysis (TGA) was performed on a Seiko TG/DTA 220 at a heating rate of 10°C/min in nitrogen and air (200 mL/min). Thin films were cast from the chloroform solution, dried at 200–250°C under vacuum over 14 days, and cut out as a strip (length = 10 mm, width = 2 mm, thickness = 0.01–0.03 mm). Young's moduli of the thin films were obtained on a Seiko TMA/SS 120C TMA/SS analyzer. The films were tested by measuring the stress and strain while applying a linear load program. For Young's modulus at 25°C, the parameters were set as: offset load = 10–20 g, load amplitude = 5–10 g, and cycling frequency = 0.05 Hz. Young's moduli (E') were obtained from the slope of the linear portion of the stress–strain plots. After the data were collected, the same film was used, without changing the parameters to Young's modulus variation with temperature, by heating to 400°C at a ramp rate of 3°C/min in static air.

Materials

Aluminum chloride, potassium carbonate, sodium hypochlorite (NaOCl), 1-fluoronaphthalene, tetramethylene sulfone ($TMSO_2$), *N*-methyl-2-pyrrolidinone (NMP), *N*-methylcaprolactam (NMC), *N*,*N*-dimethylacetamide (DMAc), phenyl sulfone, acetyl chloride, thionyl chloride, and other common organic solvents were purchased from Aldrich Chemical Co. and used as received. 1-Chloronaphthalene was fractionally distilled under vacuum (using a water aspirator). 4,4′-Isopropylidenediphenol, 4,4′-biphenol, 9,9-bis(4-hydroxyphenyl)fluorene, and 1,4-hydroquinone were purchased from Aldrich Chemical Co. and purified by recrystallization.

Monomer synthesis

4-Chloro-1-naphthoic acid

A 1 L 3-neck, round-bottomed flask equipped with a solid addition funnel and a condenser was purged with nitrogen for 20 min prior to use, and flame dried. The flask was charged with 1-chloronaphthalene (100.0 g, 0.615 mol), acetyl chloride (24.1 g, 0.30 mol), and dichloromethane (650 mL), forming a clear, colorless solution. Aluminum chloride (53.3 g, 0.40 mol) was added slowly at 0–5°C (ice bath temperature), resulting in a deep red colored mixture. The reaction mixture was stirred at this temperature for 1 h and then the temperature was raised to ca. 40–60°C and maintained for 12 h. The reaction mixture was poured into an ice-cold 10% aqueous HCl solution (500 mL) and stirred for 30 min. The organic layer was partitioned and the dark colored aqueous phase was extracted with chloroform. The combined organic extracts were washed with 5% aqueous NaOH solution and water, and then dried over $MgSO_4$. Removal of solvent afforded an oily residue, which was distilled under vacuum (20 Torr (1 Torr = 133.3 Pa), water aspirator) yielding 53.5 g (86.8%) of 4-chloro-1-acetonaphthone. To a 3 L round-bottomed flask equipped with mechanical stirrer, 4-chloro-1-acetonaphthone (52.10 g, 0.255 mol), NaOCl (1.20 L, 1.63 mol), and methanol (120 mL) were added. The mixture was stirred at 40–60°C for 12 h. The aqueous solution of sodium bisulfite (60 g in 300 mL of water) was then added, turning the reaction mixture from brown to opaque white in color. Upon acidification with 100 mL of 4 M HCl(aq), slowly added, a fluffy white precipitate was formed. The precipitate was dissolved in 5% NaOH solution. The solution was filtered to remove any residual insoluble materials and the filtrate was acidified again with 4 M HCl(aq) to give the crude product. Recrystallization from ethanol gave 4-chloro-1-naphthoic acid: 27.9 g (53.0%); mp 221–222°C (lit. (6) mp 223–224°C).

*4-Chloro-1-(4′-fluoro-1-naphthoyl)naphthalene (**6**)*

A 1 L round-bottomed flask was charged with 4-chloro-1-naphthoic acid (27.8 g, 0.14 mol) and $SOCl_2$ (40 mL) and the mixture was stirred at 80°C for 12 h. The excess $SOCl_2$ was distilled off under reduced pressure (20 Torr, water aspirator), leaving a light-brown solid residue. The crude acid chloride was vacuum distilled (1 Torr), yielding 4-chloro-1-naphthoyl chloride: 28.3 g (93.5%); mp 222–223°C (lit. (6) mp 223–224°C).

A 100 mL 3-neck round-bottomed flask was flame dried, purged with nitrogen, and charged with 4-chloro-1-naphthoyl chloride (8.00 g, 35.5 mmol), 1-fluoronaphthalene (15.3 g), and nitrobenzene (30 mL). To the solution at 0–5°C (ice bath temperature) was added aluminum chloride (4.21 g, 31.6 mmol). The resulting deep-red solution was stirred at this temperature for 1 h and then at ca. 60–70°C for 8 h. The reaction mixture was poured into an ice-cold 10% HCl – water solution (500 mL) and stirred for 30 min. The resulting oily residue was washed with 3 aliquots of methanol to remove residual nitrobenzene and then once with water, leaving a solid residue. The crude product was filtered and recrystallized from ethanol to afford monomer **6**: 6.21 g (52.2%); mp 111–112°C; IR (KBr, cm^{-1}): 1645 (C=O), 1244 (C-F), 759 (C-Cl); ^{1}H NMR (400 MHz, $CDCl_3$, Eu(fod)$_3$) δ: 9.40 (d, 1H, J_{H-H} = 4.8 Hz), 9.06 (d, 1H, J_{H-H} = 8.6 Hz), 8.46 (d, d, 1H, J_{H-H} = 8.4 Hz, $^4J_{H-H}$ = 0.8 Hz), 8.29 (m, 1H), 8.01 (m, 1H), 7.85 (d, 1H,

J_{H-H} = 7.6 Hz), 7.68 (m, 5H), 7.19 (t, 1H, J_{H-H} = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.9, 163.0, 160.4, 137.6, 136.5, 133.2, 132.9, 131.3, 130.1, 129.4, 128.6, 127.8, 127.1, 126.8, 126.5, 125.1, 125.0, 124.3, 121.1; ^{19}F NMR (300 MHz, DMSO-d_6) δ: −114.15 (s); MS (EI) (*m/z*): 334 (M^+), 299 (M^+ − Cl), 189 (M^+ − Fnaph), 173 (M^+ − Clnaph), 161 (M^+ − COnaphF), 145 (M^+ − COnaphCl), 126 (M^+ − Cl − COnaphF); HRMS calcd. for $C_{21}H_{12}OFCl$: 334.0561; found: 334.0566.

1,4-Bis(4′-fluoro-1′-naphthoyl)benzene (7)

A 500 mL 3-neck, round-bottomed flask equipped with a solid addition funnel and a condenser was purged with nitrogen for 20 min before it was charged with terephthaloyl dichloride (12.6 g, 62.1 mmol), 1-fluoronaphthalene (22.8 g, 0.16 mol), and nitrobenzene (160 mL). Once solvation was complete, aluminum chloride (21.5 g; 0.16 mol) was added to the yellow solution in portions at 0–5°C (ice bath temperature). The resulting red solution was stirred while the reaction temperature was allowed to reach room temperature during 1 h. The reaction then continued at 60–80°C for 3 h. The reaction mixture was worked up as with monomer **6** and the crude product was recrystallized three times in DMF to afford monomer **7** as yellow crystals: 17.0 g (64.8%); mp 230–231°C; IR (KBr, cm^{-1}) 1651 (C═O), 1245 (C-F); ^1H NMR (400 MHz, $CDCl_3$) δ: 8.32 (m, 1H), 8.22 (m, 1H), 7.92 (s, 2H), 7.64 (m, 3H), 7.19 (t, 1H, J_{H-H} = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.9, 102.0, 159.4, 141.7, 131.2, 129.9, 129.7 (J_{C-F} = 10 Hz), 128.5, 126.8, 125.4 (J_{C-F} = 2.0 Hz), 120.7 (J_{C-F} = 6.0 Hz), 107.9 (J_{C-F} = 21.0 Hz), ^{19}F NMR (300 MHz, TCE-d_2) δ: −114.8 (s); MS (EI) (*m/z*): 422 (M^+), 277 (M^+ − Fnaph), 249 (M^+ − COnaphF), 173 (M^+ − PhCOnaphF), 145 (M^+ − Fnaph-COPhCO); HRMS calcd. for $C_{28}H_{16}O_2F_2$: 422.1118; found: 422.1110.

Polymer synthesis

Polymerizations were all carried out in 50 mL 3-neck round-bottomed flasks equipped with a stirring bar, a Dean–Stark trap fitted with a condenser, and a nitrogen purge inlet. A typical procedure is as follows: A flask was charged with 4-chloro-1-(4′-fluoro-1′-naphthoyl)naphthalene (1.00 g, 3.00 mmol), 1,4-hydroquinone (330 mg, 3.00 mmol), potassium carbonate (829 mg, 6.00 mmol), chlorobenzene (30 mL), and $TMSO_2$ (4.8 mL, 28% w/v). The reaction temperature was rapidly raised to 140–150°C and held for 1 h. During this time, the water formed was removed with toluene and fresh toluene was introduced to the system. The temperature was then raised to 210°C, and the polymerization continued for 2 h. The reaction mixture was then cooled to about 80°C and poured into methanol (200 mL) containing 2–3 drops of concentrated HCl. The spaghetti-like polymer was collected and dissolved in chloroform (50 mL). The chloroform solution was filtered through a thin pad of Celite, and then reverse precipitated with methanol, yielding yellow fibrous polymer **3a**.

Polymer **3c**: IR (film, cm^{-1}): 1648.7 (C═O), 1238.0 (C-O-C); ^1H NMR (400 MHz, $CDCl_3$) δ: 8.60 (d, 1H, J_{H-H} = 8.2 Hz), 8.38 (d, 1H, J_{H-H} = 8.1 Hz), 7.55 (m, 2H), 7.45 (d, 1H, J_{H-H} = 8.1 Hz), 7.21 (d, 1H, J_{H-H} = 8.6 Hz), 6.98 (d, 1H, J_{H-H} = 8.6 Hz), 6.65 (d, 1H, J_{H-H} = 8.0 Hz), 1.65 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.0, 157.2, 153.8, 146.7, 133.0, 131.7, 131.7, 128.5, 128.3, 126.4, 126.0, 122.3, 119.6, 109.0, 42.3, 30.9.

Polymer **3d**: IR (film, cm^{-1}): 1654.2 (C═O), 1239.9 (C-O-C); ^1H NMR (400 MHz, $CDCl_3$) δ: 8.61 (d, 1H, J_{H-H} = 8.4 Hz), 8.37 (d, 1H, J_{H-H} = 8.0 Hz), 7.74 (d, 1H, J_{H-H} = 7.4 Hz), 7.56 (m, 2H), 7.42 (d, 1H, J_{H-H} = 6.9 Hz), 7.39 (d, 1H, J_{H-H} = 7.5 Hz), 7.34 (t, 1H, J_{H-H} = 7.4 Hz), 7.25 (t, 1H, J_{H-H} = 7.6 Hz), 7.22 (d, 1H, J_{H-H} = 8.7 Hz), 6.95 (d, 1H, J_{H-H} = 8.6 Hz), 6.65 (d, 1H, J_{H-H} = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.9, 156.9, 154.9, 150.9, 141.8, 140.0, 133.0, 131.9, 131.6, 129.6, 128.5, 127.8, 127.7, 127.5, 126.4, 126.0, 126.0, 122.2, 120.3, 119.6, 109.4, 64.4.

Polymer **5c**: IR (film, cm^{-1}): 1654.4 (C═O), 1239.1 (C-O-C); ^1H NMR (400 MHz, $CDCl_3$) δ: 8.41 (m, 2H), 7.86 (s, 2H), 7.56 (m, 2H), 7.50 (d, 1H, J_{H-H} = 8.0 Hz), 7.28 (d, 1H, J_{H-H} = 8.6 Hz), 7.05 (d, 1H, J_{H-H} = 8.5 Hz), 6.76 (d, 1H, J_{H-H} = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.4, 157.5, 153.8, 149.9, 142.2, 132.9, 130.9, 130.1, 129.4, 128.5, 127.8, 126.5, 126.5, 125.8, 122.4, 119.7, 108.8, 42.4, 31.0.

Polymer **5d**: IR (film, cm^{-1}): 1654.5 (C═O), 1238.2 (C-O-C); ^1H NMR (400 MHz, $CDCl_3$) δ: 8.35 (d, 2H, J_{H-H} = 8.1 Hz), 7.82 (s, 2H), 7.74 (d, 1H, J_{H-H} = 7.6 Hz), 7.55 (m, 2H), 7.44 (d, 1H, J_{H-H} = 8.1 Hz), 7.41 (d, 1H, J_{H-H} = 7.5 Hz), 7.35 (t, 1H, J_{H-H} = 7.4 Hz), 7.25 (m, 2H), 6.98 (d, 1H, J_{H-H} = 8.8 Hz), 6.73 (d, 1H, J_{H-H} = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.3, 157.1, 154.8, 150.9, 142.2, 142.0, 140.0, 132.8, 130.8, 130.0, 129.7, 129.3, 128.5, 127.9, 127.7, 126.6, 126.5, 126.0, 125.7, 122.3, 120.4, 119.7, 109.1.

Semicrystalline polymer ***5a***

A flask was charged with monomer **7** (1.27 g, 3.00 mmol), 1,4-hydroquinone (330 mg, 3.00 mmol), potassium carbonate (289 mg, 6.00 mmol), chlorobenzene (10 mL), and phenyl sulfone (7.82 g). The water formed in the reaction was removed together with chlorobenzene at 100-140°C. The reaction temperature was raised to 300°C and maintained for 3 h. The hot reaction mixture was poured into stirring methanol (200 mL) containing 2–3 drops of concentrated HCl. The spaghetti-like polymer was crushed up and refluxed in acetone and chloroform, respectively, for 1 h. The polymer was collected by filtration and dried in a vacuum (5 Torr) oven at 100°C for 12 h.

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