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Novel high performance poly(aryl ether ketone)s based on symmetrical naphthylene isomers

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Summary

Two new bisphenol monomers containing naphthylene groups were synthesized by a Friedel-Crafts acylation reaction followed by a demethylation reaction. Four naphthylated poly(aryl ether ketone)s (PANEKs) were successfully prepared via a typical nucleophilic substitution polycondensation. These PANEKs exhibited excellent properties including high T_gs (above 204°C) and good thermal stability (the temperature at 5% weight loss in air was above 430°C). They had improved solubility, and flexible and transparent membranes could be cast from their solutions. The good mechanical property (tensile strength of 82.2~102.8 MPa, Young's moduli of 2.1~2.4 GPa, and elongation at break of 17~31%) indicated they were strong materials. Low dielectric constant (2.8-2.9 at 1 MHz) and moisture absorptions (~0.45%) were also detected from the polymer films.

Introduction

Poly(aryl ether ketone)s (PAEKs) including poly(ether ether ketone)s (PEEKs) and poly(ether ether ketone ketone)s (PEEKKs) are a class of high performance engineering thermoplastics known for their excellent combination of chemical, physical, and mechanical properties. This class of materials is currently receiving considerable attention for potential applications in aerospace, automobile, electronic, and other high technology fields [1,2]. It is well known that commercial VICTREX PEEK™ is insoluble in common organic solvents, which limits its utility in some applications. Developing soluble PAEKs, without sacrificing their thermal stability, is a topic of interest [3,4].

Due to their unique structure, naphthylated aromatic polymers have been synthesized by several research groups [5-9]. They found these polymers normally have high glass transition temperatures (T_g) because of the presence of bulky and rigid naphthylene groups. In addition, the solubility of the polymers could be improved by introducing naphthylene moieties. There is a continuous demand for aromatic polymers to use as low dielectric constant (low k) materials [10,11]. Generally, two strategies have been adopted to decrease the dielectric constant of polymers. One is to incorporate fluorinated moieties into polymers. For example, fluorinated polymers, such as fluorinated poly(aryl ether)s, usually have good solubility and high thermal stability [12]. However, HF may be emitted when the fluorinated polymers are processed at high temperature, which may damage the device and instruments [13]. Another way is to incorporate bulky substituents, such as fluorenyl and adamantly groups, into polymers [14,15]. This method avoids some of the problems associated with fluorinated polymers, such as high cost, environmental issues and HF emission.

In this work, bulky naphthylene groups were introduced into PAEKs based on the polymerization of two new naphthylene-containing monomers. Their properties, such as thermal properties, solubility, tensile property and also dielectric constant were thoroughly investigated.

Experimental

Materials

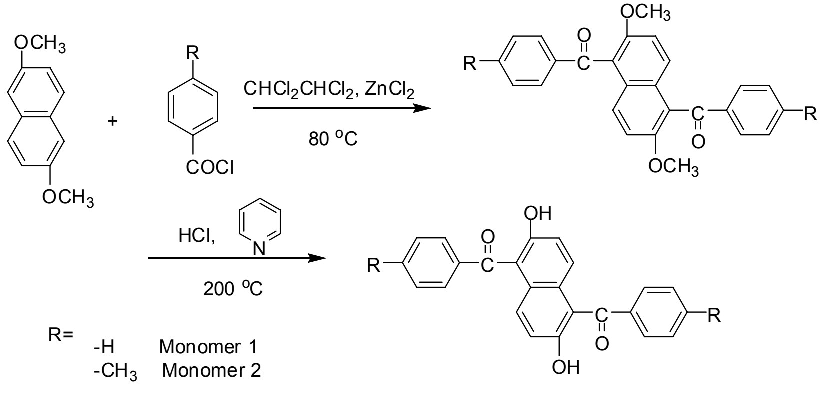
4-Methybenzoyl chloride, 3-methybenzol chloride, 4,4'-difluorobenzophenone, and 1,4-bis(4-fluorobenzoyl)benzene were prepared in our laboratory. Tetramethylene sulfone (TMS) was purified by distillation under reduced pressure before use. All other chemicals used for the synthesis of monomers and polymers were obtained from commercial sources and used without further purification.

Instruments

FTIR (KBr) was recorded on a Nicoler Impact 410 Fourier transform infrared spectrometer. The ^{1}H NMR spectra were recorded using a Bruker 510 NMR spectrometer with tetramethylsilane as the internal reference. Differential scanning calorimetry (DSC) measurements were performed on a METTLER TOLEDO DSC 821e instrument at the heating rate of 10°C /min under nitrogen. Thermal gravimetric analyses (TGA) were performed using a PERKIN ELMER TGA-7 thermal analyzer system at the heating rate of 10°C /min in Air. The dielectric constants of thin polymer films were measured on an HP 1645B/4194A impedance gain-phase analyzer with a round-board electrode.

Synthesis of monomers and polymers

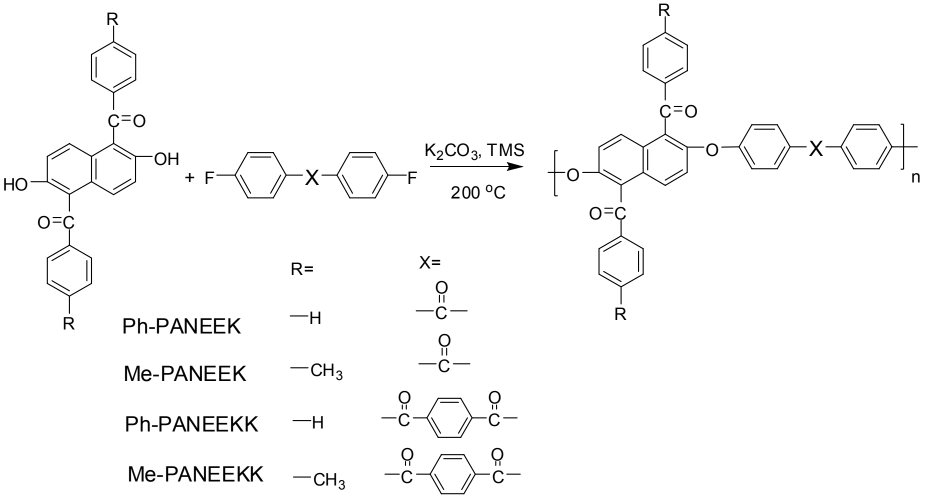
The bisphenol monomers, 1,5-bisbenzoyl-2,6-dihydroxynaphthalene (Monomer 1) and 1,5-bis(4-methylbenzoyl)-2,6-dihydroxynaphthalene (Monomer 2), were synthe-



Scheme 1. Synthetic route of Monomer 1 and 2.

sized in two-step by a Friedel-Crafts acylation reaction followed by a demethylation reaction, as shown in Scheme 1.

Benzoyl-containing naphthylated PEEK (Ph-PANEEK), PEEKK (Ph-PANEEKK), methylbenzol-containing naphthylated PEEK (Me-PANEEK), and PEEKK (Me-PANEEKK) were prepared in TMS at high temperature by a typical nucleophilic aromatic substitution (Scheme 2).



Scheme 2. Synthesis of the naphthylated PANEKs.

Preparation of samples

Thin films (~ 0.1mm thickness) were cast from $CHCl_3$ solution of polymers onto flat glass plates, and dried at room temperature for 24 h. The films were finally obtained after drying at 80°C for 24 h in a vacuum oven.

Results and Discussion

Two naphthyl-containing bisphenol monomers with symmetrical chemical structures (Monomer 1 and 2) were successfully synthesized in high purity and high yield via a two-step reaction route. The Friedel-Crafts acylation reaction was performed based on 2,6-dimethoxynaphthalene and $ZnCl_2$ was selected as the catalyst. It was noted that complex products were obtained when $AlCl_3$ was used as the catalyst. The resulting structures were well characterized by FTIR, MS and ^1H NMR. The ^1H NMR spectrum of Monomer 2 is shown in Figure 1.

The polymerization of the new bisphenol monomers with stoichiometric amounts of two different difluoro monomers, 4,4'-difluorobenzophenone, and 1,4-bis(4-fluorobenzoyl)benzene, was carried out in the presence of excess potassium carbonate as the base in TMS, and toluene was used for the azeotropic removal of water. The mixture was reacted under reflux for 2 h, and the generated water was removed through a Dean-Stark trap. After that, the reaction temperature was increased to 200°C. Viscous polymer solutions were readily obtained in 4-6 h. In a previous study reported by Ueda et al., only low-molecular-weight (Mn 4,800~13,500) naphthylated polymers could be prepared due to the existence of rigid and bulky naphthylene moieties [7]. In our present work, the existence of bulky pendant groups in the monomers did not have a significant effect on the polymerization. The resulting polymers were obtained with high molecular weight (Mn 21,000~86,000), as shown in Table 1. The structures of the polymers were confirmed by ^{1}H NMR spectra, and a typical ^{1}H NMR spectrum is shown in Figure 2.

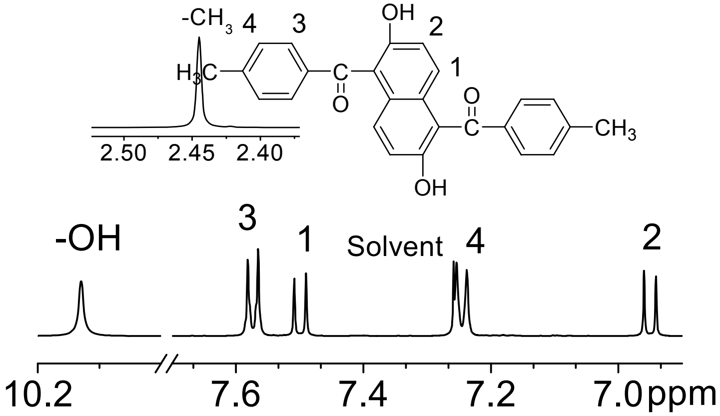


Figure 1. ^{1}H NMR spectrum of Monomer 2 in $CDCl_3$.

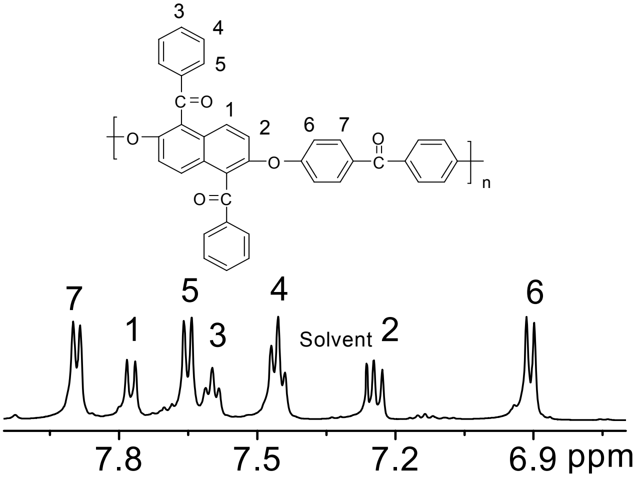


Figure 2. ^{1}H NMR spectrum of Ph-PANEEK in $CDCl_3$.

The thermal properties of the polymers were evaluated by DSC and TGA. As expected, all the polymers showed high T_gs in the range of 204-213°C, which was much higher than that of PEEK^{TM} (143°C). These polymers also had good thermal stability. The temperature at 5% weight loss of fully aromatic Ph-PANEEK and Ph-PANEEKK were above 470°C in air, which were significantly higher than Me-PANEEK (431°C) and Me-PANEEKK (442°C). This was caused by the poor thermal stability of methyl groups of Me-PANEEK and Me-PANEEKK (Figure 3).

Table 1 Molecular weights and properties of the polymers

Polymer	Mn [a]	Mw/Mn [b]	T_g (°C) [c]	TD_5 (°C) [d]	k [e]	Water Sorption (%) [f]
Ph-PANEEK	31300	2.1	204	480	2.91	0.46
Ph-PANEEKK	21600	2.5	205	472	2.90	0.42
Me-PANEEK	52900	3.0	211	431	2.85	0.43
Me-PANEEKK	85900	3.2	213	442	2.89	0.41

[a] Number-average molecular weight determined by GPC.
[b] Polydispersity.
[c] Glass transition temperature from the second heating cycle of DSC.
[d] Temperature at 5% weight loss.
[e] Dielectric constant at 1 MHz.
[f] Calculated from the difference in the weights before and after boiling the polymer films in water for 2 h.

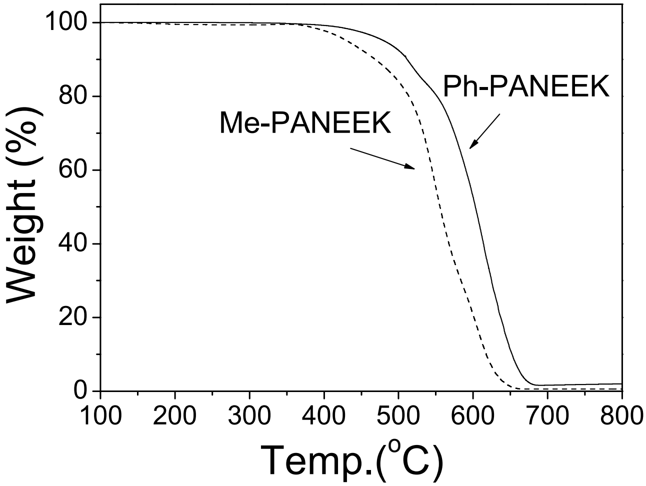


Figure 3. TGA curves of Ph-PANEEK and Me-PANEEK in air.

All of the PANEKs showed improved solubility and were readily soluble in aprotic polar solvents such as NMP, DMAc and DMF as well as in the less polar solvents such as chloroform and THF at room temperature. Hence, flexible and transparent membranes could be cast from their solution. The samples had tensile strength of 82.2~102.8 MPa, Young's moduli of 2.1~2.4 GPa, and elongation at break of 17~31%, indicating they were strong materials.

It was noted that the dielectric constant of conventional PEEK was 3.3 at 1 MHz. The dielectric constants of PANEK were in the range of 2.8-2.9 at 1 MHz, which were comparable to the partly fluorinated polymers (2.7-2.8 at 1 MHz) reported by us [16,17]. There were two related factors that could explain the observed effect of chemical structure on the dielectric properties of polymers. Firstly, the bulky side groups attached to the polymer main chains apart, which might lead to looser packing of molecular chains and more free volume and therefore lower dielectric constant. In general, the incorporation of polar groups, such as carbonyl groups, would lead to increased dielectric constant. In our system, the incorporation of polar carbonyl groups did not greatly increase dielectric constant. A possible explanation was that strong electron-withdrawing —CO— groups in the symmetrical β-position of the naphthalene ring might restrict electrons within the plane. Therefore, the polarization of the polymers by the exterior electric field was decreased.

Moisture absorption is always associated with dielectric constant, and the water uptakes calculated from the difference in the weights before and after boiling the vacuum-dried polymer films in water for 2 h were in the range of 0.41% ~ 0.46%.

Conclusions

Novel PAEKs containing symmetric naphthylene moieties were successfully prepared from two types of naphthylated monomers. In comparison with PEEK^{TM}, these polymers had higher T_gs, improved solubility and formed strong films by solution casting. The naphthalylated PANEKs were studied as low k materials, and they showed low dielectric constants and low water absorption. They may be good candidates for high-temperature membranes as microelectronic dielectrics.

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