

# Poly(ether ether ketone)s and Poly(ether ether ketone ketone)s Containing Cardo Decahydronaphthalene Groups: Synthesis and Characterization

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**ABSTRACT:** New poly(ether ether ketone)s and poly(ether ether ketone ketone)s were synthesized by polycondensation of each of the three bisphenols, viz., 4,4'-(octahydro-2(1H)-naphthylidene)bisphenol, 4,4'-(octahydro-2(1H)-naphthylidene)bis-3-methylphenol, and 4,4'-(octahydro-2(1H)-naphthylidene)bis-3,5-dimethylphenol with 4,4'-difluorobenzophenone and 1,3-bis(4-fluorobenzoyl)benzene in a mixture of *N,N*-dimethylacetamide and toluene [1 : 1 (v/v)] in the presence of anhydrous potassium carbonate. Inherent viscosities of poly(ether ether ketone)s and poly(ether ether ketone ketone)s were in the range 0.32–0.80 dL/g and number-average molecular weights were in the range 16,100–55,900 g/mol. Poly(ether ether ketone)s and poly(ether ether ketone ketone)s were soluble in organic solvents such as dichloromethane, chloroform, tetrahydrofuran, *meta*-cresol, pyridine, and 1-methyl-2-pyrrolidinone at room tempera-

ture and could be cast into tough, transparent, and flexible films from their chloroform solutions. Wide angle x-ray diffraction measurements revealed the amorphous nature of poly(ether ether ketone)s and poly(ether ether ketone ketone)s. The glass transition temperature poly(ether ether ketone)s and poly(ether ether ketone ketone)s were in the range 185–251°C. The temperature at 10% weight loss, determined from thermogravimetric analysis, of poly(ether ether ketone)s and poly(ether ether ketone ketone)s in nitrogen atmosphere was in the range 462–493°C indicating their good thermal stability. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1607–1613, 2011

**Key words:** poly(ether ether ketone)s; poly(ether ether ketone ketone)s; polycondensation; bisphenol; cardo decahydronaphthalene; thermal properties

## INTRODUCTION

Poly(ether ether ketone)s or PEEKs and poly(ether ether ketone ketone)s or PEEKKs are well recognized as high performance engineering thermoplastics as they possess high modulus and toughness and good thermal and chemical resistance.<sup>1–4</sup> Therefore, PEEKs and PEEKKs are currently receiving considerable attention for potential applications in aviation, automobile manufacturing, electronic/electrical, medical care, fuel cell, gas separation, and food processing sectors. PEEKs and PEEKKs can be prepared via electrophilic or nucleophilic substitution reaction.<sup>2,3</sup> The electrophilic route using Friedel-Crafts acylation reaction has some limitations because of mechanistic problems. The nucleophilic route has been the most commonly used method to

prepare PEEKs and PEEKKs which involves generation of an ether linkage by nucleophilic aromatic substitution as a polymer forming reaction and uses dihalide monomers in which the carbonyl group serves as the activating moiety.<sup>5–9</sup>

In spite of their excellent performance, the processing and even the synthesis of PEEKs and PEEKKs has been limited because of their low solubility in common organic solvents resulting from their aromatic structure and semicrystallinity due to the high packing tendency of ketone and phenyl ether linkages in the main chain of PEEKs and PEEKKs. Many approaches have been tried toward the improvement of solubility and processability of PEEKs and PEEKKs which include the incorporation of noncoplanar structures,<sup>10–12</sup> pendent groups, and the alternation of the order and ratio of ether-ketone linkages<sup>13,14</sup> as well as *meta* and *para*-phenyl substitution.<sup>15</sup> The incorporation of cardo groups such as 9,9-diarylfuorene,<sup>16</sup> acenaphthenequinone,<sup>17</sup> spirodilactam,<sup>18</sup> phthalein,<sup>19</sup> and xanthene<sup>19</sup> into the backbone of poly(arylene ether ketone)s is an attractive approach toward enhanced solubility and glass transition temperature. In our previous work, we reported the synthesis and characterization of polyesters

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containing cardo decahydronaphthalene groups with enhanced solubility and glass transition temperature.<sup>20</sup> In continuation of our work on processable high performance polymers, we wish to report herein synthesis of new PEEKs and PEEKKs by polycondensation of the three bisphenols, viz., 4,4'-(octahydro-2(1H)-naphthylidene)bisphenol (NBP), 4,4'-(octahydro-2(1H)-naphthylidene)bis-3-methylphenol (*o*-NBP), and 4,4'-(octahydro-2(1H)-naphthylidene)bis-3,5-dimethylphenol (DM-NBP) with 4,4'-difluorobenzophenone (DFB) and 1,3-bis(4-fluorobenzoyl)benzene (BFB) in a mixture of *N,N*-dimethylacetamide and toluene [1 : 1 (v/v)] in the presence of anhydrous potassium carbonate. PEEKs and PEEKKs were characterized by inherent viscosity measurements, solubility tests, FT-IR, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR spectroscopy, x-ray diffraction, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). The effects of incorporation of cardo decahydronaphthalene groups and the presence of asymmetric dimethyl and symmetric tetramethyl substitution on bisphenol rings on the properties of PEEKs and PEEKKs such as solubility and thermal behavior was investigated.

## EXPERIMENTAL

### Materials

4,4'-(Octahydro-2(1H)-naphthylidene)bisphenol (NBP), 4,4'-(octahydro-2(1H)-naphthylidene)bis-3-methylphenol (*o*-NBP), and 4,4'-(octahydro-2(1H)-naphthylidene)bis-3,5-dimethylphenol (DM-NBP) were synthesized as described in our previous work.<sup>20</sup> 4,4'-Difluorobenzophenone and 1,3-bis(4-fluorobenzoyl)benzene (Aldrich) were recrystallized from toluene before use. Anhydrous potassium carbonate (S.D. Fine) was dried at 150°C for 24 h under reduced pressure. *N,N*-Dimethylacetamide (DMAc) was dried over calcium hydride and distilled under reduced pressure. *N*-Methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), *meta*-cresol, pyridine, chloroform, and tetrahydrofuran (THF) were purified as per literature procedures.<sup>21</sup>

### Measurements

Inherent viscosity of PEEKs and PEEKKs was measured with 0.5% (w/v) solution of polymer in chloroform at 30 ± 0.1°C using an Ubbelohde suspended level viscometer. Solubility of PEEKs and PEEKKs was determined at 3 wt % concentration in various solvents at room temperature or upon heating at 70°C for 3 h. FT-IR spectra were recorded using films on a Perkin-Elmer 883 spectrophotometer. <sup>1</sup>H-NMR spectra for PEEKs and PEEKKs were recorded on a Bruker 400 MHz spectrometer using CDCl<sub>3</sub> as a solvent. Molecular weights of PEEKs and

PEEKKs were measured on ThermoFinnigan make gel permeation chromatography (GPC), using the following conditions: column, polystyrene-divinylbenzene (10<sup>5</sup>–50 Å); detector, RI; room temperature. Polystyrene was used as the calibration standard. Polymer sample (5 mg) was dissolved in 5 mL chloroform and filtered through 0.2 μ SS-filter. X-ray diffraction patterns of PEEKs and PEEKKs were obtained on a RigakuDmax 2500 X-ray diffractometer. Thermogravimetric analysis was performed on Perkin-Elmer TGA-TA5000R system at a heating rate of 10°C/min under nitrogen atmosphere. Sample weight taken was ~ 5 mg. DSC analysis was carried out on TA Instruments DSC Q10 at a heating rate of 20°C/min in nitrogen atmosphere.

### Polymer synthesis

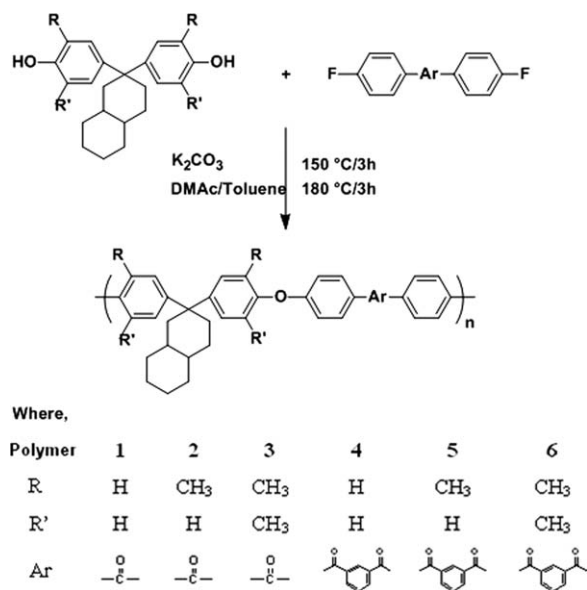
A representative procedure for the synthesis of PEEK-1 is given as follows. Into a 100 mL three-necked round bottom flask equipped with a reflux condenser, a nitrogen inlet tube, a magnetic stirring bar, and a Dean-Stark trap were charged 4,4'-(octahydro-2(1H)-naphthylidene)bisphenol, (1 g, 3.10 mmol), 4,4'-difluorobenzophenone, (0.67 g, 3.10 mmol), potassium carbonate (0.51 g, 3.72 mmol), DMAc (10 mL), and toluene (10 mL). The reaction mixture was heated with stirring at 150°C for 3 h. Toluene was used to remove the water by azeotropic distillation. Toluene was removed after 3 h and temperature of the reaction mixture was raised to 180°C and kept at that temperature for 3 h. The viscous reaction mixture was poured into methanol (100 mL); the precipitated polymer was filtered and washed several times with water to remove the metal salt. The polymer was dissolved in chloroform and precipitated into 100 mL methanol. The polymer was filtered, washed with methanol, and dried under reduced pressure at 80°C for 24 h.

A similar procedure was followed for the synthesis of other PEEKs and PEEKKs.

## RESULTS AND DISCUSSION

### Synthesis of PEEKs and PEEKKs

Scheme 1 depicts the synthesis of PEEKs and PEEKKs containing cardo decahydronaphthalene groups. A series of PEEKs and PEEKKs were prepared by polycondensation of the three bisphenols, viz., NBP, *o*-NBP, and DM-NBP with two dihalide monomers, viz., DFB and BFB in a mixture of DMAc and toluene [1 : 1, (v/v)] in the presence of anhydrous potassium carbonate. The results of synthesis of PEEKs and PEEKKs are presented in Table I. PEEKs and PEEKKs were isolated as white fibrous materials with inherent viscosities in the range 0.32–0.80 dL/g indicating the formation of polymers with



Scheme 1 Synthesis of PEEKs and PEEKKs.

medium to reasonably high molecular weights. This is also reflected in the results of measurement of molecular weights of PEEKs and PEEKKs by GPC (Table I). Number average molecular weights ( $M_n$ ) were in the range 16,100–55,900 g/mol with polydispersity index in the range 1.9–2.5. However, the molecular weight values provided by GPC should not be taken as absolute as the calibration of GPC was carried out using polystyrene standards. PEEKs and PEEKKs could be cast into tough, transparent, and flexible films from their solution in chloroform.

### Characterization of PEEKs and PEEKKs

FT-IR and  $^1\text{H-NMR}$  spectra were used to confirm the formation of PEEKs and PEEKKs. FT-IR spectrum showed characteristic band of the carbonyl group at  $1656\text{ cm}^{-1}$  and ether group at  $1243\text{ cm}^{-1}$ .  $^1\text{H-NMR}$  spectrum of PEEK-3 derived from DM-NBP and DFB is reproduced in Figure 1. Multiplets were observed in the range 7.65–7.85 ppm and 6.70–6.88 ppm for protons *ortho* and *meta* to ketone group, respectively. The multiplicity of peaks suggests the presence of

constitutional isomers in PEEKs containing cardo decahydronaphthalene group. In brief, DFB moiety experiences different magnetic environments based on the way DM-NBP was condensed with DFB. It can be predicted that axial and equatorial phenyl rings in the bisphenol molecule can enchain with dihalide in the manner; axial-axial, axial-equatorial, equatorial-axial, and equatorial-equatorial resulting in the observed NMR splitting patterns. The singlet observed at 6.96 ppm was assigned to proton *ortho* to methyl group of the axial aromatic ring, while the singlet observed at 7.09 ppm was assigned to proton *ortho* to methyl group of the equatorial aromatic ring. The two distinct singlets at 2.07 and 2.12 ppm were observed for methyl group protons attached to axial and equatorial phenyl rings, respectively. The methylene and methine protons of the decahydronaphthalene ring displayed a multiplet over the range 1.20–2.50 ppm.

### Polymer solubility

The solubility data of PEEKs and PEEKKs in organic solvents at 3.0% (w/v) is shown in Table II. It is well known that conventional PEEKs and PEEKKs do not dissolve in common organic solvents. In sharp contrast, PEEKs and PEEKKs containing cardo decahydronaphthalene groups exhibited excellent solubility in common organic solvents. All the polymers were soluble at room temperature in solvents such as dichloromethane, chloroform, tetrahydrofuran, *meta*-cresol, pyridine, and NMP. The polymers were sparingly soluble on heating at 70°C for 3 h in solvents such as DMF and DMSO. The enhanced solubility of polymers could be attributed to the incorporation of cardo decahydronaphthalene groups, which disturbs the close packaging of the polymer chain and leads to the increased free volume, which in turn, facilitates the penetration of the solvent molecules resulting in improved solubility.

### X-ray diffraction studies

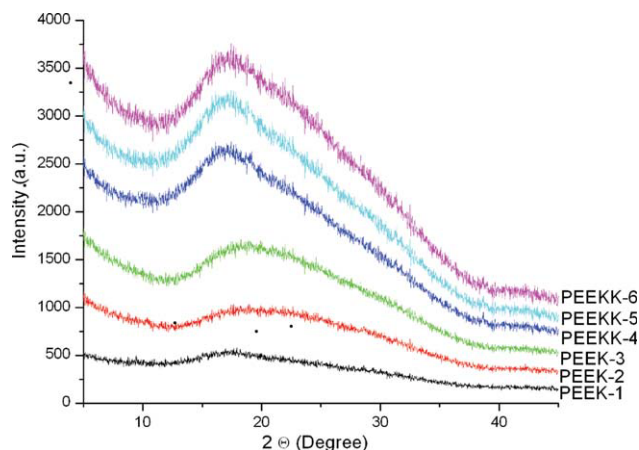
The crystallinity of PEEKs and PEEKKs was evaluated by wide angle x-ray diffraction (WAXD)

TABLE I  
Synthesis of PEEKs and PEEKKs

Polymer	Bisphenol	Dihalide	Yield, (%)	$\eta_{inh}^a$ (dL/g)	Molecular weight (g/mol)		
					$M_n$	$M_w$	$M_w/M_n$
PEEK-1	NBP	DFB	97	0.60	40,670	82,840	2.0
PEEK-2	<i>o</i> -NBP	DFB	98	0.32	17,000	33,900	2.0
PEEK-3	DM-NBP	DFB	98	0.35	16,100	36,100	2.2
PEEKK-4	NBP	BFB	99	0.80	55,900	114,000	2.5
PEEKK-5	<i>o</i> -NBP	BFB	97	0.60	29,800	75,300	2.5
PEEKK-6	DM-NBP	BFB	98	0.68	45,100	102,000	2.3

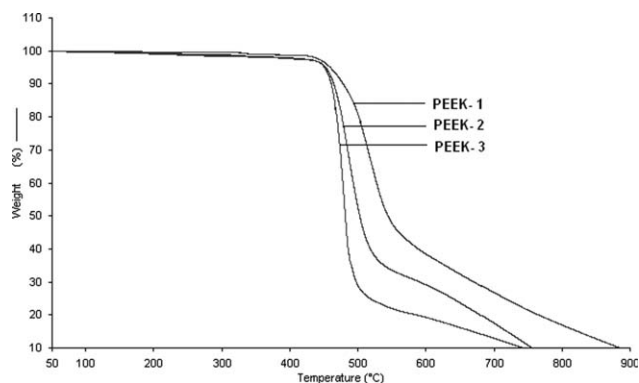
<sup>a</sup>  $\eta_{inh}$  was measured with 0.5% (w/v) solution of PEEKs and PEEKKs in chloroform at  $30 \pm 0.1^\circ\text{C}$ .





**Figure 2** TG curves of PEEK-1, PEEK-2, and PEEK-3 [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).].

and DM-NBP with DFB were in the range 201–251°C, whereas the  $T_g$  values of PEEKKs derived from bisphenol and BFB were in the range 185–224°C.  $T_g$  value of PEEK based on NBP-DFB was



**Figure 3** DSC curves of PEEKs and PEEKKs in nitrogen.

higher than  $T_g$  value (173–175°C) of corresponding PEEK obtained by polycondensation of cyclohexanone-based bisphenol (bisphenol-Z) and DFB.<sup>22</sup>

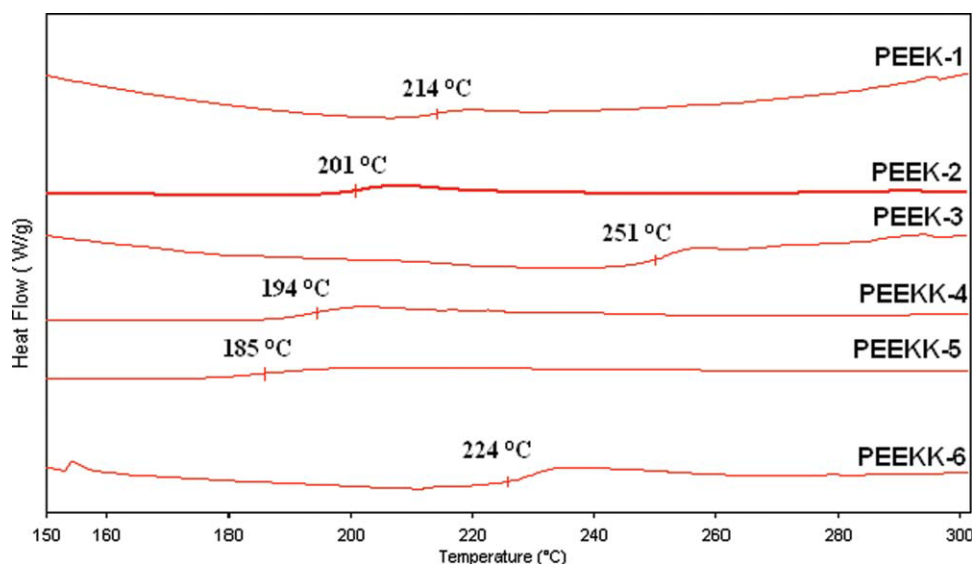
The substitution of phenylene hydrogens of PEEKs and PEEKKs containing “cardo” groups with methyl groups exhibited significant effect on their glass transition temperature. The effects of the methyl substituents on bisphenol moiety *ortho* to the ether-connecting

**TABLE III**  
Thermal Properties of PEEKs and PEEKKs in Nitrogen

Polymer	Polymer structure	$T_g$ (°C) <sup>a</sup>	IDT (°C) <sup>b</sup>	$T_{10}$ (°C) <sup>b</sup>
PEEK-1		214	455	479
PEEK-2		201	455	462
PEEK-3		251	459	465
PEEKK-4		194	454	493
PEEKK-5		185	462	473
PEEKK-6		224	460	464

<sup>a</sup> Measured on DSC at a heating rate of 20 °C/min.

<sup>b</sup> Measured on TGA at a heating rate of 10°C / min in nitrogen.



**Figure 4** X-ray diffractograms of PEEKs and PEEKKs [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).].

group on  $T_g$  were evaluated (Table III). The PEEK-1 with no substituent, PEEK-2 with dimethyl, and PEEK-3 with tetra methyl substituent on the bisphenol ring showed  $T_g$  values 214, 201, and 251°C, respectively. Similarly, the PEEKK-4 with no substituent, PEEKK-5 with dimethyl, and PEEKK-6 with tetra methyl substituent on the bisphenol ring showed  $T_g$  values of 194, 185, and 224°C, respectively. DSC data indicated that the PEEKs and PEEKKs containing symmetric tetramethyl substitution resulted in higher  $T_g$  values than those of the corresponding dimethyl substituted and unsubstituted PEEKs and PEEKKs. In polymers, asymmetric dimethyl substitution resulted in lowering of  $T_g$  value than that of unsubstituted PEEKs and PEEKKs. The consideration of segmental symmetry is useful in explaining this behavior. PEEKs containing symmetric tetramethyl substitution resulted in a large chain stiffening effect and therefore their  $T_g$  values were higher than that of the corresponding dimethyl substituted and unsubstituted PEEKs and PEEKKs. The dimethyl substitution leads to an asymmetric segment which can result in less efficient chain packing and hence more free volume that led to relatively easier chain mobility of polymer segments in comparison with symmetrical substituted and unsubstituted PEEKs and PEEKKs, ultimately leading to decrease in  $T_g$ . A similar observation was reported for polyesters in our previous work<sup>20</sup> and also it has been reported previously for polyarylates, polysulfones, polycarbonates, etc.<sup>23–25</sup>

### CONCLUSIONS

A series of new poly(ether ether ketone)s and poly(ether ether ketone ketone)s containing cardo decahydronaphthalene groups was synthesized by poly-

condensation of each of the three bisphenols, viz., NBP, *o*-NBP, and DM-NBP with DFB and BFB. The presence of constitutional isomerism resulting from the different enchainment of the phenyl rings of bisphenol monomers along the polymer chain was revealed by NMR analysis of PEEKs and PEEKKs. PEEKs and PEEKKs containing cardo decahydronaphthalene groups showed excellent solubility pattern in organic solvents such as chloroform, dichloromethane, tetrahydrofuran, *meta*-cresol, pyridine, and *N*-methyl-2-pyrrolidinone at room temperature. Tough, transparent, and flexible films of PEEKs and PEEKKs could be cast from their solutions in chloroform. Wide angle x-ray diffraction patterns indicated that PEEKs and PEEKKs containing cardo decahydronaphthalene groups were amorphous in nature. Due to the segmental symmetry, high glass transition temperatures were observed for tetra methyl substituted PEEKs and PEEKKs as compared to the dimethyl substituted PEEKs and PEEKKs.  $T_{10}$  values of PEEKs and PEEKKs containing cardo decahydronaphthalene groups were in the range 462–493°C in nitrogen atmosphere indicating their good thermal stability.

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