

Synthesis and Characterization of Organo-Soluble Poly(ether ether ketone)s and Poly(ether ether ketone)s Containing Pendant Pentadecyl Chains

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ABSTRACT: Poly(ether ether ketone)s and poly(ether ether ketone)s containing pendant pentadecyl chains were synthesized by polycondensation of each of the two bisphenol monomers *viz.*, 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and 1,1-bis(4-hydroxyphenyl)-3-pentadecyl cyclohexane with activated aromatic dihalides namely, 4,4'-difluorobenzophenone, and 1,3-bis(4-fluorobenzoyl)benzene in a solvent mixture of *N,N*-dimethylacetamide and toluene, in the presence of anhydrous potassium carbonate. Polymers were isolated as white fibrous materials with inherent viscosities and number average molecular weights in the range 0.70–1.27 dL g⁻¹ and 76,620–1,36,720, respectively. Poly(ether ether ketone)s and poly(ether ether ketone)s were found to be soluble at room temperature in organic solvents such as chloroform, dichloromethane, tetrahydrofuran, and pyridine and could be cast into tough, transparent, and flexible films from their solutions in chloroform. Wide

angle X-ray diffraction patterns exhibited a broad halo at around $2\theta = \sim 19^\circ$ indicating that the polymers containing pentadecyl chains were amorphous in nature. In the small-angle region, diffuse reflections of a typically layered structures resulting from the packing of pentadecyl side chains were observed. The temperature at 10% weight loss, obtained from TG curves, for poly(ether ether ketone)s and poly(ether ether ketone)s were in the range 416–459°C, indicating their good thermal stability. A substantial drop in glass transition temperatures (68–78°C) was observed for poly(ether ether ketone)s and poly(ether ether ketone)s due to “internal plasticization” effect of flexible pendant pentadecyl chains. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 3689–3695, 2011

Key words: poly(arylene ether)s; polyethers; poly(ether ketone)s; pentadecyl; alkyl side-chain; cashew nut shell liquid; CNSL; renewable

INTRODUCTION

Poly(aryl ether ketone)s or PAEKs are a family of semicrystalline, high temperature, high performance engineering thermoplastics displaying a useful combination of physical, thermal, and mechanical properties and find applications in aerospace, automobile, medical devices, food processing, gas separation membranes, fuel cell, and electronics industries.^{1–21} The commercial PAEKs (PEK, PEKK, PEEK, PEKEKK) only differ from each other by their ether/ketone (E/K) ratio in the chain. PAEKs are usually prepared by nucleophilic displacement or Friedal-Crafts acylation (electrophilic polycondensation).²² However, in spite of their excellent performance, the processing and even the synthesis of PAEKs has been restricted because of their low solu-

bility in common organic solvents resulting from their high crystallinity. To overcome these limitations, a great deal of research efforts on PAEKs has been centered on the introduction of pendant groups such as phenyl, halogen, trifluoromethyl, ditrifluoromethylphenyl, and bromomethyl to improve the solubility and processability.^{14,15,20,23–32} The introduction pendant alkyl groups via bisphenols was demonstrated by Cassidy and coworkers to improve the solubility and processability of PAEKs.³³

Recently, we have reported a series of difunctional monomers containing pendant pentadecyl chain which were utilized for the synthesis of high performance polymers such as aromatic polyesters, polyamides, poly(amideimide)s, and polyimides.^{34–38} It was demonstrated that the presence of pendant pentadecyl chains improved the solubility and processability of these polymers and provided a large temperature difference between the glass transition temperature and the initial decomposition temperature. In continuation of our ongoing-efforts to synthesize processable high performance polymers, we wish to report herein synthesis of poly(ether ether ketone)s (PEEKs) and poly(ether ether ketone)s (PEEKKs) containing pendant pentadecyl

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chains by nucleophilic polycondensation of each of the two bisphenols *viz*, 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane (BHPE) and 1,1-bis(4-hydroxyphenyl)-3-pentadecyl cyclohexane (BHPC) with commercially available aromatic dihalide monomers *viz*; 4,4'-difluorobenzophenone (DFB) and 1,3-bis(4-fluorobenzoyl)benzene (BFB). PEEKs and PEEKKs were characterized by inherent viscosity measurements, solubility tests, FTIR, ^1H NMR, ^{13}C NMR spectroscopy, gel permeation chromatography (GPC), wide angle X-ray diffraction, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). The influence of pendant pentadecyl chains on polymer properties such as solubility and thermal behavior was investigated.

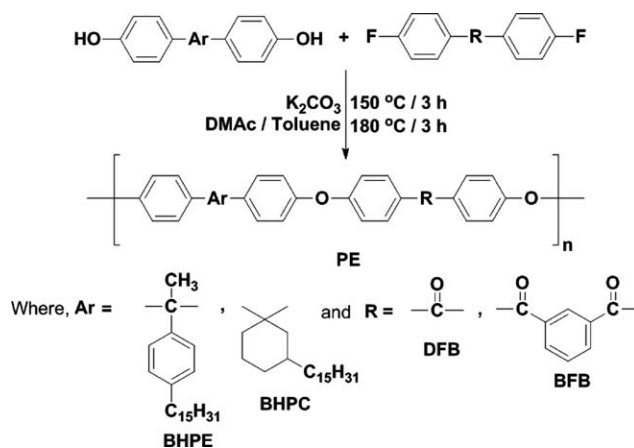
EXPERIMENTAL

Materials

The bisphenol monomers *viz*; 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane (BHPE) and 1,1-bis(4-hydroxyphenyl)-3-pentadecylcyclohexane (BHPC) were synthesized starting from cashewnut shell liquid (CNSL) using procedure described in our previous work.^{34,37,39,40} The 4,4'-difluorobenzophenone (DFB) and 1,3-bis(4-fluorobenzoyl)benzene (BFB) (Aldrich, USA) were recrystallized from toluene before use. Anhydrous potassium carbonate (S.D. Fine, India) 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. The solvents were of reagent grade quality and were purified prior to use according to the reported procedures.⁴¹

Measurements

Inherent viscosity of PEEKs and PEEKKs was measured with 0.5% (w/v) solution of polymer in chloroform at 30°C \pm 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 on heating. FTIR spectra were recorded using polymer films on a Perkin-Elmer Spectrum GX spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker 200 or 400 MHz spectrometer using CDCl_3 as a solvent. Molecular weights of PEEKs and PEEKKs were measured on ThermoFinnigan make gel permeation chromatograph (GPC), using the following conditions: Column—polystyrene-divinylbenzene (10⁵–50 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 polymers were obtained on a Rigaku



Scheme 1 Synthesis of PEEKs and PEEKKs containing pendant pentadecyl chains.

Dmax 2500 X-ray diffractometer at a tilting rate of 2° min⁻¹. Thermogravimetric analysis was performed on TGA—TA5000R system at a heating rate of 15°C min⁻¹ under nitrogen atmosphere. Sample weight taken was ~ 5 mg. DSC analysis was carried out on TA Instruments DSC Q10 at a heating rate of 10°C min⁻¹ in nitrogen atmosphere.

Synthesis of PEEKs and PEEKKs

A representative procedure for the synthesis of Peek (PE-I) is 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 BHPE (500 mg, 1 mmol), DFB, (210 mg, 1 mmol), potassium carbonate (160 mg, 1.2 mmol), *N,N*-dimethylacetamide (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 methanol. The polymer was filtered, washed with methanol, and dried under reduced pressure at 80°C for 24 h.

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

RESULTS AND DISCUSSION

Polymer synthesis

Scheme 1 illustrates synthesis of PEEKs and PEEKKs containing pendant pentadecyl chains. PEEKs and

TABLE I
Synthesis and Properties of PEEKs and PEEKKs Containing Pendant Pentadecyl Chains

Polymer	Bisphenol	Dihalide	Yield (%)	η_{inh} (dL g ⁻¹) ^a	GPC ^b			Thermal behavior data			
					M_n (g mol ⁻¹)	M_w (g mol ⁻¹)	M_w/M_n	T_0^c (°C)	T_{10}^d (°C)	Weight residue at 900°C (%)	T_g^e (°C)
PE-I	BHPE	DFB	96	1.07	1,14,070	2,43,530	2.1	413	440	38	68
PE-II	BHPE	BFB	93	0.70	76,620	1,70,100	2.2	392	429	39	75
PE-III	BHPC	DFB	95	1.27	1,25,130	3,33,230	2.6	417	459	17	69
PE-IV	BHPC	BFB	96	1.0	1,36,720	3,33,870	2.4	378	416	21	78

^a η_{inh} was measured with 0.5% (w/v) solution of PEEKs and PEEKKs in CHCl₃ at 30°C ± 0.1°C.

^b Measured by GPC in chloroform, polystyrene was used as a calibration standard.

^c Initial decomposition temperature.

^d Temperature at which 10% weight loss is observed.

^e Glass transition temperature.

PEEKKs were synthesized by polycondensation of bisphenols with activated aromatic dihalides in a mixture of polar aprotic solvent, *N,N*-dimethylacetamide, and azeotropic solvent toluene, in the presence of anhydrous potassium carbonate. Polymers were isolated by precipitating viscous reaction mixture in excess methanol. The results of polymerization are presented in Table I. PEEKs and PEEKKs were isolated as white fibrous materials with inherent viscosities (η_{inh}) in the range 0.70–1.27 dL g⁻¹. PEEKs and PEEKKs were soluble in chloroform and their molecular weights were determined by GPC. The results of GPC measurements are presented in Table I. The number average molecular weights (M_n) of PEEKs and PEEKKs were in the range 76,620–1,36,720 with polydispersity index in the range 2.1–2.6. Inherent viscosity and GPC data indicated the formation of reasonably high molecular weight polymers. 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. Tough, transparent and flexible films of PEEKs and PEEKKs could be cast from their solutions in chloroform.

Polymer characterization

The chemical structure of the PEEKs and PEEKKs was confirmed by FTIR, ¹H NMR, and ¹³C NMR spectroscopy. A representative FTIR spectrum of PEEK (PE-I) derived from BHPE and DFB is reproduced in Figure 1. A characteristic band of the carbonyl group was observed at around 1656 cm⁻¹ and the aromatic ether linkage stretching vibration was observed at around 1250 cm⁻¹. A band at around 720 cm⁻¹ (methylene rocking vibration) is indicative of the presence of long aliphatic chain. Figure 2(a,b) show ¹H NMR and ¹³C NMR spectra of PEEKK (PE-II) derived from BHPE and BFB as an example. A triplet at 8.1 ppm could be assigned to a proton “a”

flanked by two carbonyl groups. Protons “b” appeared as doublet of doublet in the range 7.90–7.99 ppm, while proton “d” exhibited a triplet at 7.55 ppm. The four aromatic protons “c,” *ortho* to carbonyl group appeared as a doublet at 7.81 ppm. Aromatic protons on bisphenol moiety appeared as a multiplet over the range 6.94–7.17 ppm. Methyl protons attached to a quaternary carbon appeared as a singlet at 2.18 ppm. The benzylic –CH₂ appeared as a triplet at 2.56 ppm. The methylene protons β to aromatic ring exhibited a multiplet in the range 1.40–1.75 ppm. The other methylene protons displayed a multiplet over the range 1.12–1.25 ppm. Methyl protons of the aliphatic chain appeared as a triplet at 0.85 ppm. In ¹³C NMR spectrum of PE-II derived from BHPE and BFB, carbonyl carbon was observed at 194.51 ppm. The carbons adjacent to ether linkage “b” and “c” appeared at 161.92 and 153.36 ppm, respectively. The carbon flanked by two carbonyl groups appeared at 138.14 ppm and the quaternary carbon was observed at 51.49 ppm. The

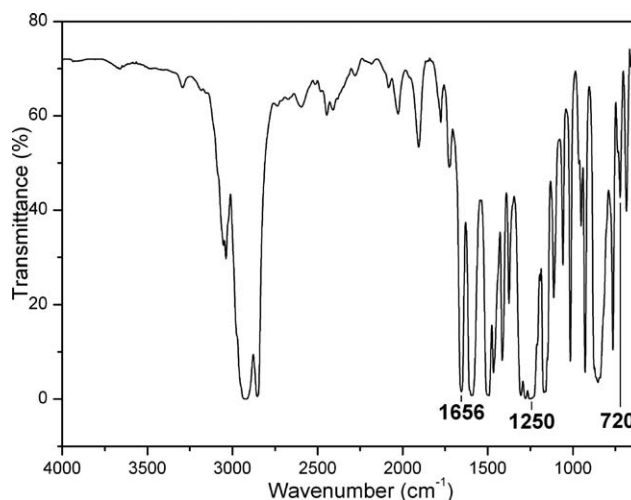


Figure 1 IR spectrum of PEEK derived from BHPE and DFB (PE-I).

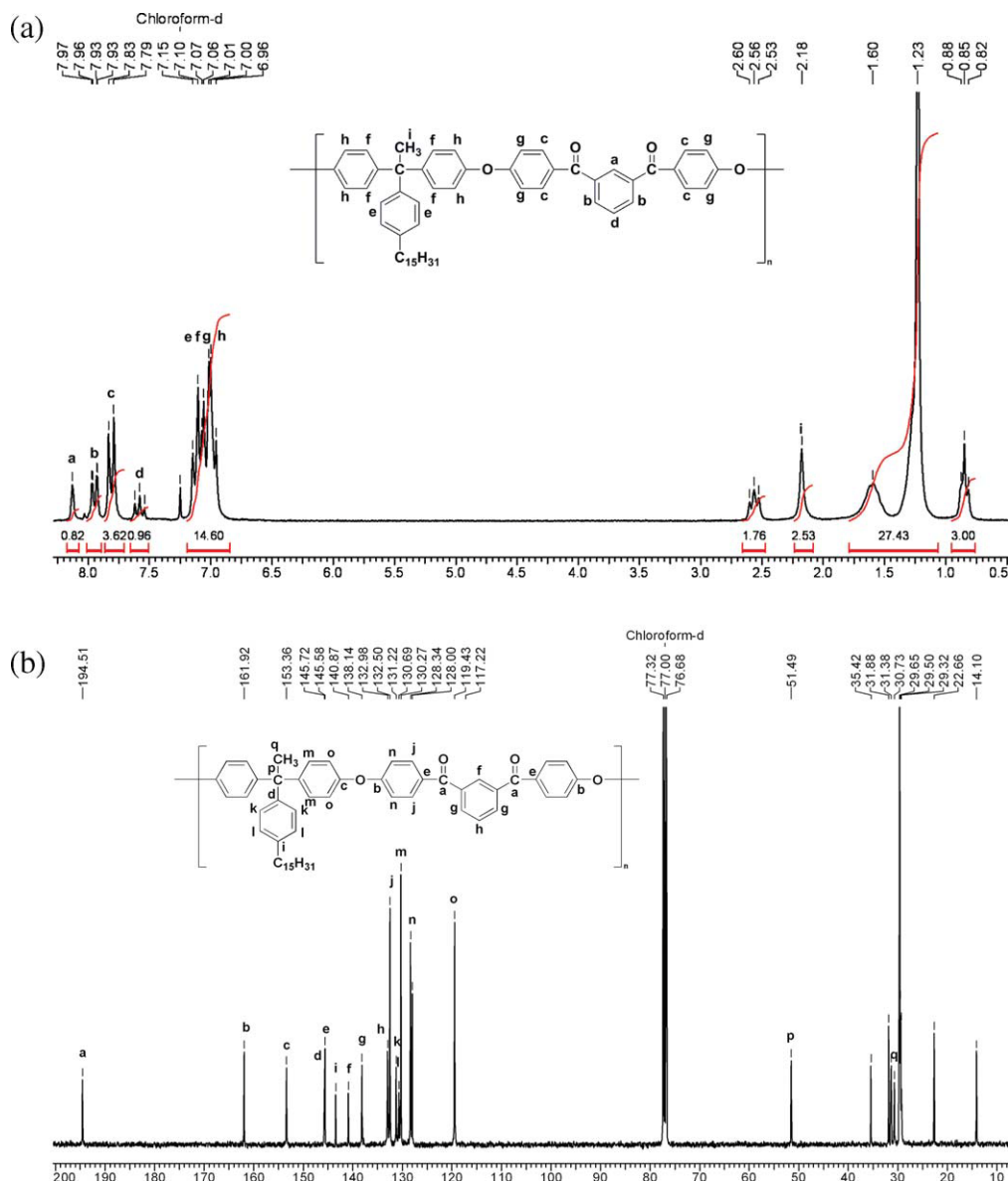


Figure 2 (a) ¹H NMR spectrum of PEEKK derived from BHPE and BFB (PE-II) in CDCl₃ (b) ¹³C NMR spectrum of PEEKK derived from BHPE and BFB (PE-II) in CDCl₃. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

spectral data corresponding to other carbon atoms was in good agreement with the proposed structure. The peak assignments in ¹³C NMR spectrum were confirmed by DEPT spectrum.

Solubility of PEEKs and PEEKKs

Solubility of PEEKs and PEEKKs was tested in various organic solvents at 3 wt % concentration and the data is summarized in Table II. It is well known that

TABLE II
Solubility Data of PEEKs and PEEKKs Containing Pendant Pentadecyl Chains

Polymer	Bisphenol	Dihalide	CHCl ₃	DCM	THF	DMF	DMAc	NMP	Pyridine	<i>m</i> -Cresol	DMSO
PE-I	BHPE	DFB	++	++	++	+-	+-	+-	++	++	--
PE-II	BHPE	BFB	++	++	++	+-	+-	+-	++	++	--
PE-III	BHPC	DFB	++	++	++	+-	+-	+-	++	+-	--
PE-IV	BHPC	BFB	++	++	++	+-	+-	+-	++	+-	--

++: soluble at room temperature; +-: soluble on heating; --: insoluble even on heating.

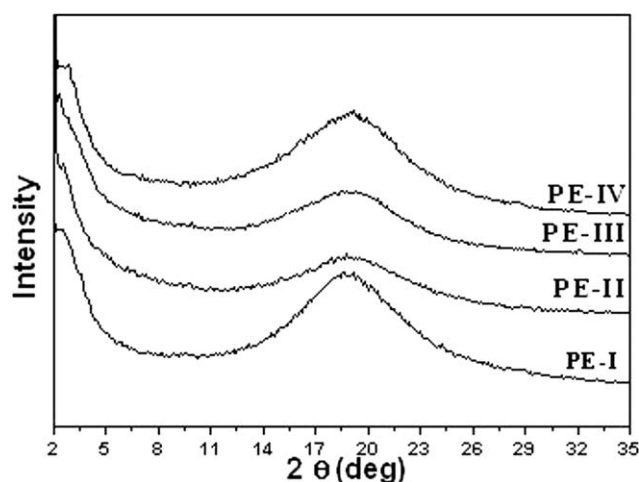


Figure 3 X-ray diffractograms of PEEKs and PEEKKs containing pendant pentadecyl chains.

conventional poly(ether ether ketone) derived from bisphenol-A and 4,4'-difluorobenzophenone can not be dissolved in common organic solvents.⁴² In sharp contrast, the PEEKs and PEEKKs containing pendant pentadecyl chains reported in the present study were soluble in common organic solvents such as chloroform, dichloromethane, tetrahydrofuran, and pyridine at room temperature. All polymers were soluble upon heating in polar aprotic solvents such as *N,N*-dimethylacetamide, 1-methyl-2-pyrrolidinone and *N,N*-dimethylformamide. Solubility in common organic solvents allows unique fabrication opportunities to PEEKs and PEEKKs. These PEEKs and PEEKKs could be considered as good candidates for applications such as gas separation and microelectronic devices where the combination of solubility plus good thermal properties is desired.

The good solubility of these polymers could be attributed to the introduction of the pendant pentadecyl chains, which disturbed the close packing of the polymer chains and led to the increase in the free volume. Therefore, it was easy for the solvent to penetrate through the polymer chains. The presence of pentadecyl chain also provided additional "handle" for interaction with solvents thus aiding in the improved solubility characteristics.

X-ray diffraction studies of PEEKs and PEEKKs

In the X-ray diffraction patterns of PEEKs and PEEKKs (Fig. 3), a broad halo at around $2\theta = \sim 19^\circ$ was observed. The introduction of pendant pentadecyl chain into the polymer backbone hinders the chain packing resulting in amorphous nature of these polymers, which is also reflected in their enhanced solubility. In the small-angle region at around $2\theta = \sim 2-3^\circ$, a diffuse peak was observed for PEEKs and PEEKKs. This suggests the presence

of loosely developed layered structure in PEEKs and PEEKKs, in which the main chains were separated with disordered side chains. These layered structures developed due to the packing of pentadecyl chains. A similar observation has been reported in our earlier work for polyamides, polyimides and poly(amideimide)s containing pendant flexible side chains.^{35-38,43-45}

Thermal properties of PEEKs and PEEKKs

In the present study, thermal stability of the PEEKs and PEEKKs was determined by thermogravimetric analysis (TGA) at a heating rate of $15^\circ\text{C min}^{-1}$ under nitrogen. The initial decomposition temperature (T_0), the temperature at 10% weight loss (T_{10}) and the weight residue at 900°C for polymers are given in Table I. Thermogravimetric (TG) curves of PEEKs and PEEKKs are shown in Figure 4. All the PEEKs and PEEKKs showed similar pattern of decomposition. T_{10} values, obtained from TG curves, for PEEKs and PEEKKs were in the range $416-459^\circ\text{C}$ under nitrogen atmosphere indicating their good thermal stability. The T_0 and T_{10} values seem to be dictated by the structure of both the difluoride monomer and the bisphenol used. BFB-based polymers exhibited lower T_0 and T_{10} values than the corresponding polymers based on DFB. T_{10} values of PEEKs based on 1,1-bis(4-hydroxyphenyl)cyclohexane and BPA are reported to be 496 and 505°C , respectively, in air.⁴⁶ The lower thermal stability of PEEKs based on BHPE and BHPC compared to those of PEEKs based on 1,1-bis(4-hydroxyphenyl)cyclohexane and BPA could obviously be attributed to the presence of aliphatic pentadecyl chains in the former. These results are consistent with the observations reported previously for PEEKs bearing long

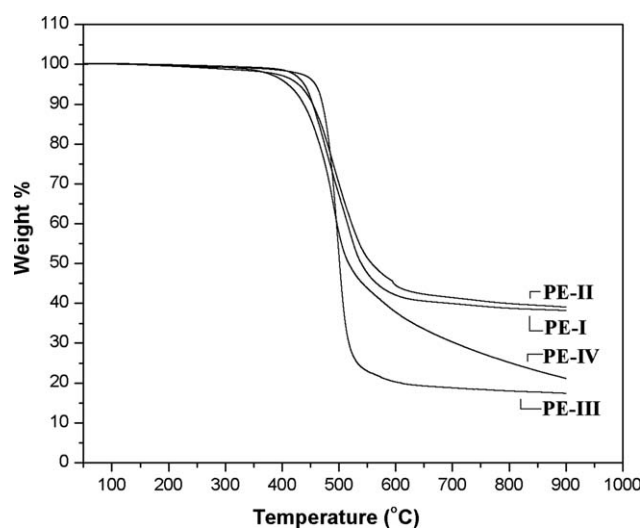


Figure 4 TG curves of PEEKs and PEEKKs containing pendant pentadecyl chains.

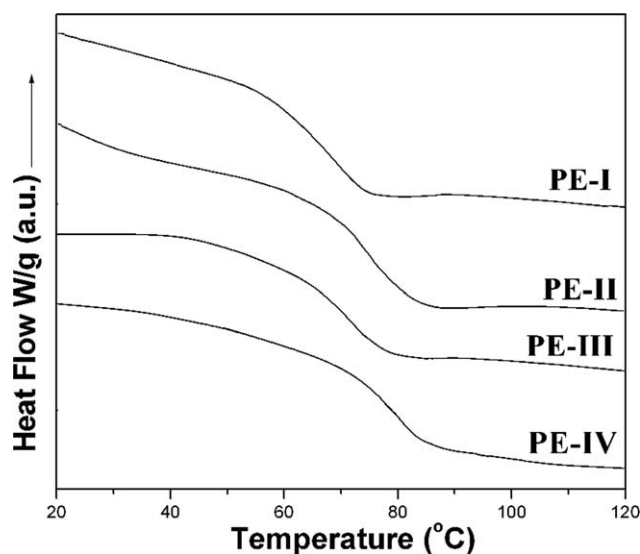


Figure 5 DSC curves of PEEKs and PEEKKs containing pendant pentadecyl chains.

alkyl side chains.³³ The weight residue of polymers at 900°C was in the range 16–39% and is dictated by the structure of the bisphenol used. The weight residue at 900°C was lower in case of BHPC-based polymers than the analogous polymers based on BHPE which could be attributed to the presence of cyclohexyl ring in addition to the aliphatic pentadecyl chain thus resulting into higher content of aliphatic units.

Glass transition temperature (T_g) of the PEEKs and PEEKKs was evaluated by differential scanning calorimetry (DSC). T_g values were obtained from second heating scans of polymer samples at a heating rate of 10°C min⁻¹. DSC curves for PEEKs and PEEKKs containing pendant pentadecyl chains are reproduced in Figure 5 and the T_g values are given in Table I. PEEKs and PEEKKs containing pendant pentadecyl chains exhibited T_g values in the range 68–78°C. T_g value of PEEK based on 1,1-bis(4-hydroxyphenyl)cyclohexane is reported to be 173–175°C,⁴⁶ while T_g value of PEEK based on BHPC was found to be 69°C. The substantial drop in T_g values of PEEKs and PEEKKs based on BHPE and BHPC could be attributed to the presence of flexible pendent pentadecyl chains which act as an ‘internal plasticizer’. It has been reported that as the plasticizer content increases the free volume of the polymer increases which eventually decreases the glass transition temperature.⁴⁷ A large difference between glass transition (68–78°C) and initial decomposition temperature (378–417°C) was observed. This offers PEEKs and PEEKKs a wide processing window.

CONCLUSIONS

PEEKs and PEEKKs containing pendant pentadecyl chains were synthesized by polycondensation of

bisphenols *viz*, 1,1,1-[bis(4-hydroxyphenyl)-4'-penta-decylphenyl]ethane and 1,1-bis(4-hydroxyphenyl)-3-pentadecyl cyclohexane with activated aromatic dihalides in a mixture of *N,N*-dimethylacetamide and toluene, in the presence of potassium carbonate. Organo-soluble and reasonably high molecular weight PEEKs and PEEKKs were obtained which could be cast into tough, transparent and flexible films from their chloroform solutions. PEEKs and PEEKKs were amorphous in nature. The loosely developed layered structure formation was observed due to the packing of pentadecyl chains. The T_{10} values, for PEEKs and PEEKKs, were in the range 416–459°C indicating their good thermal stability. Glass transition temperature (68–78°C) of PEEKs and PEEKKs was lowered substantially due to “internal plasticization” effect of pentadecyl chain in polymer backbone.

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