

Synthesis and Characterization of New Soluble Poly (Arylene Ether Ketone)s

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Abstract

A novel bisfluoro monomer was synthesized in two steps:

1) 9-ethylcarbazole obtained from 9H-Carbazole and 1-bromoethane, and

2) a new 3, 6-bis-4-fluorobenzoyl-9-ethylcarbazole monomer was obtained from 9-ethylcarbazole and 4-fluorobenzoylchloride; it was then used to prepare novel Poly (Arylene Ether Ketone)s (PAEKs). FTIR and ¹HNMR methods were used to characterize the synthesized monomers and polymers. Further, solubility tests showed that PAEKs were generally soluble in a wide range of solvents including Dimethyl Acetamide (DMAc), N-Methylpyrrolidone (NMP), Dimethyl Sulfoxide (DMSO) and H₂SO₄. Thermo Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) indicate that the synthesized PAEKs showed only 10% weight loss in air up to 410°C and were essentially amorphous.

Keywords: Carbazole; Polycondensation; Poly (arylene ether ketone); Solubility; Thermal properties

Abbreviations:

PAEKs: Poly (Arylene Ether Ketone)s; DMAc: Dimethyl Acetamide; NMP: N-Methylpyrrolidone; DMSO: Dimethyl Sulfoxide; TGA: Thermo Gravimetric Analysis; DSC: Differential Scanning Calorimetry.

Introduction

Poly (arylene ether)s form a major class of high performance polymeric materials with excellent thermal and mechanical properties [1-3]. These polymers consist of aromatic rings and ether linkages. Amongst various methods for synthesis of poly (arylene ether)s, one method is widely used: nucleophilic displacement of an activated dihalo and dinitro compound with activated bisphenoxide salt at high temperature [4-6]. Despite the necessity to activate the leaving groups by an electron withdrawing group (e.g., sulfone, ketone or imide groups) at the para-position, Johnson, demonstrated that the presence of these groups results in synthesis of high molecular weight poly ethers [4]. Within aromatic poly (arylene ether)s, PAEK pose a quality performance in thermo-oxidative, electrical and chemical resistance properties [7-9]. This makes them suitable candidates as advanced materials in aerospace, electronics and nuclear fields industry [10-15]. Despite different approaches in synthesis of these polymers, they are mainly synthesized using insolation by the nucleophilic aromatic substitution (S_N Ar) between bisphenols and aromatic bis-halide salt high reaction temperatures (typically >150°C) and in the presence of weak bases such as K₂CO₃ and Na₂CO₃ [2,16]. Conducting polymers containing conjugated double bonds along the backbone due to their

flexibility, ease of fabrication and lightness of weight possesses great superiority over the inorganic semiconductors [17]. Due to these advantages, they have been investigated as the materials of electronics, optoelectronics, and photonics. These polymers are also potential candidates for a wide spectrum of commercial applications ranging from catalysts for photo-electrochemical processes, electrode materials, microelectronic devices, and organic batteries to electrochromic display devices [17,18]. 9H-carbazole is a heterocyclic compound with photo conducting properties and high electron-donating characteristics that is used in the synthesis of poly condensation or polymerization polymers. In addition to interesting electro-optical and photochemical properties, this compound donates high thermal stability to polymer due to its conjugated structure [18]. 9H-carbazole can be easily functionalized on the 3,6-, [19] 2,7-, [20] or N-positions, [21] it is covalently linked into polymeric systems, both in the main chain as building blocks [22] and side-chain as pendant group [23].

In the present study, we synthesize new PAEKs with improved thermal properties. This procedure consists of three major steps:

1) 9-ethylcarbazole is derived via N-alkylation onto 9H-carbazole.

2) Friedel-Crafts Acylation on 3, 6-position of 9-ethylcarbazole results in the new monomer, bis-halide.

3) The polymer is produced by poly-condensation between the new bis-halide monomer and three aromatic diols (resorcinol, hydroquinone and naphthalene diols).

Subsequently, the synthesized polymer is analyzed in terms of its thermal and also solubility properties.

Experimental

Materials and instruments

9H-Carbazole, ethylbromide, 4-fluorobenzoyl chloride, 18-crown-6 and all other chemicals were purchased from Fluka (Switzerland). ¹HNMR spectra were recorded on a Bruker advance DRX 500 MHz instrument, using DMSO-d₆ and CdCl₃ as solvent and tetramethylsilane as an internal standard. FTIR spectra were recorded on a Bruker, Vector 22 spectrometer, using KBr pellets. TGA under air atmosphere and heating rate of 20 K/min in the range of 43-650°C using TGA-Q500 TA and DSC from room temperature to 280°C at 10 K/min under N₂ atmosphere using DSC-Discovery TA were performed. Inherent viscosity ($\eta_{inh} = \ln \eta_{rel}/c$) of polymers was determined for solutions of 0.1, 0.2 and 0.5 g/dl in DMAc at 25°C using an Ubbelohde viscometer.

Synthesis of 9-ethylcarbazole

Inside a 250 mL two-neck round-bottom flask equipped with a magnetic stirrer bar, 9H-Carbazole (20 mmol), KOH (30 mmol) and 18-Crown-6 (20 mg as phase transfer catalysis) were added to 40 ml of toluene and refluxed for 30 min. The solution of ethylbromide (30 mmol) compound was gradually added into 20 ml of toluene and then into the reaction mixture (following Koyuncu procedure [24]). The mixture was stirred at 110°C for 6 h and then cooled to the room temperature. Then, the reaction mixture was poured into 150 ml of ethanol and stripped off by a rotary evaporator. The product was recrystallized from methanol and dried in vacuum desiccators. The reaction yield was estimated to be about 93%.

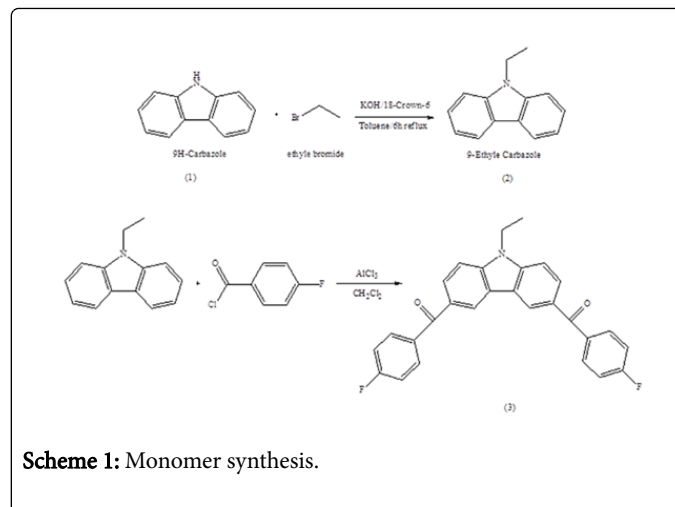
FTIR (cm⁻¹): (aromatic C-H stretching) 3035.81; (aliphatic C-H stretching) 2857.48; (-CH₂ stretching) 2917.36; (-CH₃ stretching) 2964.77; (C=C ring stretching) 1564; (aliphatic C-N) 1092.08; (aromatic C-N) 1296.67; (aromatic C-H bend out of plane) 682.06-714.15.

Synthesis of monomer (3, 6-bis-4-fluorobenzoyl-9-ethylcarbazole)

Inside a 250 ml three-neck round-bottom flask equipped with a magnetic stirrer bar, a Nitrogen inlet, and an acid trap, 0.39 gr (2 mmol) 9-ethylcarbazole, 0.66 gr (5 mmol) aluminum chloride and 50 ml dichloromethane were charged. The temperature of the reaction mixture was maintained at -5°C and 0.6 ml (5 mmol) 4-Fluorobenzoyl chloride was added drop-wise (following Ghaemy procedure [25]). After complete addition, the medium was stirred for 2 h at 0°C and for two more hours at room temperature. Upon completion of the reaction (as witnessed by TLC test), the mixture was poured into water and extracted with ethyl acetate. The organic layer was concentrated under reduced pressure and dried at 70°C under vacuum. The yield of the viscous greenish liquid was 0.7 gr (80%).

FTIR (cm⁻¹): (aromatic C-H stretching) 3045.12; (aliphatic C-H stretching) 2843.42; (-CH₂ stretching) 2919.55; (-CH₃ stretching) 2963.04; (C=O stretching) 1657; (C-F stretching) 1263.63; (C=C ring stretching) 1573.41; (aliphatic C-N) 1096; (aromatic C-N) 1299; (aromatic C-H bend out of plane) 889.86- 815.62.

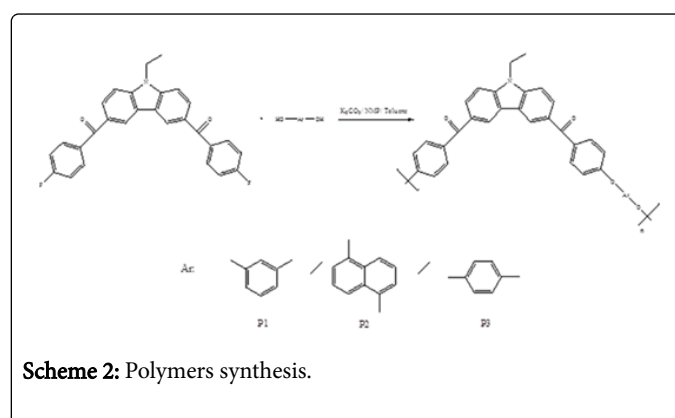
¹HNMR (500 MHz, CdCl₃, δ in ppm): 1.31-1.52 (t, 3H, CH), 4.44-4.45 (q, 2H, CH), 7.55-7.56 (m, 2H, Ar-H), 7.92-7.94 (t, 4H, Ar-H), 8.03-8.09 (d, 2H, Ar-H), 8.15-8.18 (t, 4H, Ar-H), 8.63 (s, 2H, Ar-H).



Scheme 1: Monomer synthesis.

Synthesis of polymer

According to the reported procedure in the literature, [26] polymerization reactions were carried out in a 50 ml, three-neck round-bottom flask equipped with a Nitrogen inlet, a stirrer bar, and a Dean-Stark trap fitted with condenser. The reactions were conducted under constant flow of Nitrogen. A representative polymerization procedure is as follows: the flask was charged with equimolar amounts of 3, 6-bis-4-fluorobenzoyl-9-ethylcarbazole and diol (2 mmol each), K₂CO₃ (4.2 mmol), NMP (20 ml) and toluene (40 ml). The mixture was then heated to reflux (140-150°C, oil bath temperature) for 2-3 h to remove the water azeotropically with toluene. After removal of the toluene from the Dean-Stark trap, the reaction temperature was increased to 180°C and maintained for another 6 h. After cooling to room temperature, the polymer was precipitated from about 500 ml of methanol containing 10 ml of HCl. Fibrous solids were isolated. These products were washed several times in boiling distilled water to remove any inorganic impurities followed by methanol and dried under vacuum at 65°C for overnight.



Scheme 2: Polymers synthesis.

FTIR (cm⁻¹): P1: (aromatic C-H stretching) 3048.10; (aromatic C-N) 1280.09; (C=C ring stretching) 1562.81; (aliphatic C-N) 1092.17; (C=O stretching) 1658.69; (C-O-C stretching) 1229.66.

P2: (aromatic C-H stretching) 3043.92; (aromatic C-N) 1278.60; (C=C ring stretching) 1565.93; (aliphatic C-N) 1093.63; (C=O stretching) 1658.70; (C-O-C stretching) 1214.30.

P3: (aromatic C-H stretching) 3044.98; (aromatic C-N) 1280.52; (C=C ring stretching) 1566.78; (aliphatic C-N) 1095.04; (C=O stretching) 1658.73; (C-O-C stretching) 1158, 1197.

$^1\text{H NMR}$ (500 MHz, DMSO-d_6 , δ in ppm):

P1: 1.18-1.34 (t, 3H, CH), 4.5 (q, 2H, CH), 7.20-8.74(Ar-H).

Results and Discussion

Monomer synthesis and characterization

The new bisfluoro monomer containing 9-ethylcarbazole as internal unit and 4-fluorobenzoyl chloride as terminal units was synthesized in two steps. From a synthetic standpoint, there are generally three distinct methods for incorporating carbazole units into a polymeric material: polymerization with the carbazole's 1) 3, 6-positions, [27-30] 2) 2,7-positions [31] or 3) 9-position. Since it is desirable that 4-fluorobenzoyl chloride do not react with the 9-position, at first 9-position was functionalized to lose its reactivity. This step consists of aliphatic nucleophilic substitution reaction. Yellowish needle-like 9-ethylcarbazole crystals obtained from Friedel-Crafts alkylation reaction between 9H-carbazole and 1-bromoethane in the presence of KOH and 18-crown-6 phase transfer catalyst in toluene solvent. In order to purify the product, recrystallization by methanol was done (Scheme 1). The production of 9-ethylcarbazole was confirmed by FTIR (Figure 1).

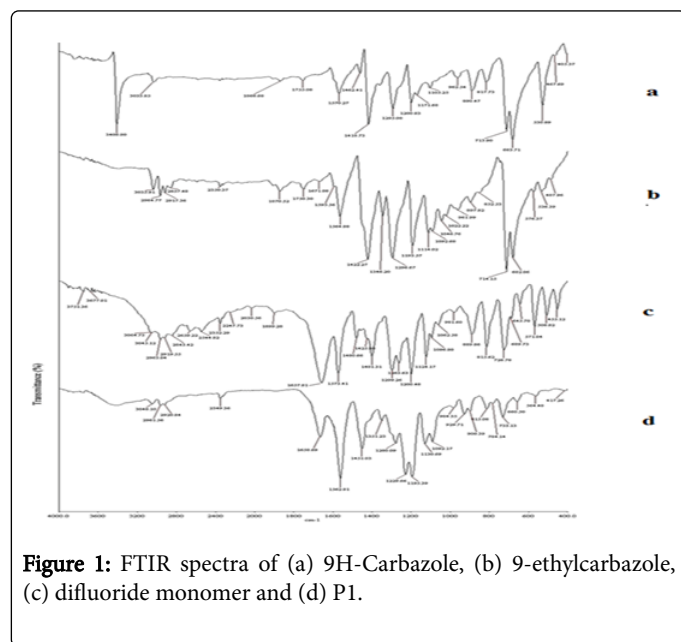


Figure 1: FTIR spectra of (a) 9H-Carbazole, (b) 9-ethylcarbazole, (c) difluoride monomer and (d) P1.

Carbazole as a result of its N-H bond shows an absorption peak at 3408 cm^{-1} . This peak has been replaced by absorption peaks at 1092 and 1114 cm^{-1} which attribute to aliphatic C-N bond. Also, some absorption peaks are detectible at 2917 , 2964 and 2857 cm^{-1} which attribute to CH_2 , CH_3 and aliphatic C-H, respectively. In the next step, Friedel-Crafts acylation reaction was performed between 9-ethylcarbazole and 4-fluorobenzoyl chloride in the presence of aluminum chloride catalyst in dichloromethane solvent (Scheme 1); the reaction product was then separated using ethyl acetate. The reason behind situation of 4-fluorobenzoyl chloride on the 3,6- position of 9-ethylcarbazole can be explained in the following way: 9-ethylcarbazole can react at 3,6- or 2,7- positions, however from organic chemistry

viewpoint preparation of 2,7-dihalosubstituted carbazoles is not as straightforward as the synthesis of 3,6-substituted samples [32]. In addition, reaction between 9-ethylcarbazole and 4-fluorobenzoyl chloride is an electrophilic aromatic substitution and meta position of amino group of carbazole, i.e., 2,7- positions, cannot be functionalized directly by this method [32]. Therefore, 4-fluorobenzoyl chloride situated on the 3,6- position of 9-ethylcarbazole. The chemical structure of monomer has been confirmed using FTIR and NMR spectra. FTIR spectra of monomer has absorption peaks of C=O and C-F at 1657 and 1263 cm^{-1} , respectively. In the $^1\text{H NMR}$ spectra of monomer (Figure 2), associated signals of CH_3 and CH_2 groups are detectible in 1.31-1.52 and 4.44-4.45 ppm. More chemical shift of CH_2 results from the higher electronegativity of Nitrogen atom that has been connected to CH_2 in this sample.

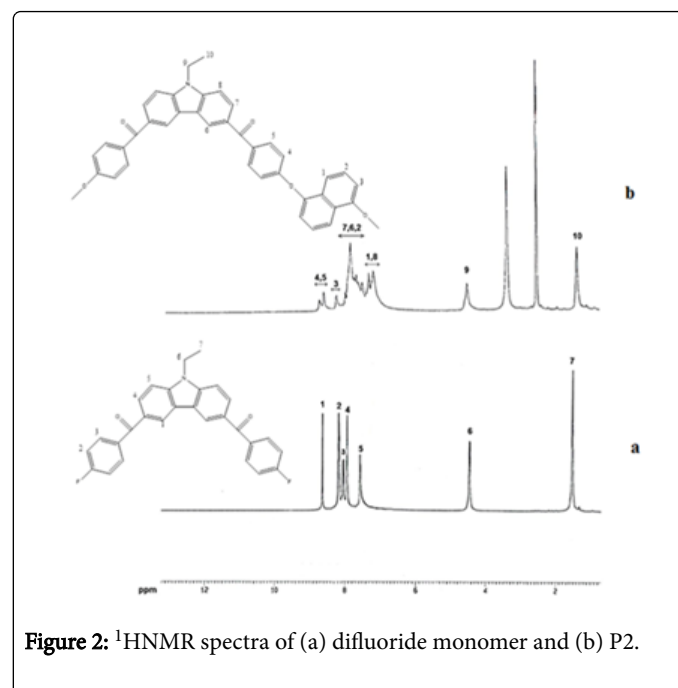


Figure 2: $^1\text{H NMR}$ spectra of (a) difluoride monomer and (b) P2.

Since there is no proton in the vicinity of proton of carbon 1, its signal has been appeared as singlet, on the other hand signal related to the proton of carbon 5 as a result of presence of protons of alkyl group and also carbon 4 appears as multiple.

Polymer synthesis and characterization

In the polymerization step, new difluoride monomer in the presence of K_2CO_3 and NMP solvent in a poly-condensation process reacted with 3 types of bisphenol to production of 3 new PAEKs (Scheme 2). At the primary steps of reaction, toluene was used to eliminate zeotropic water that had being produced as a side-product during reaction. A Dean-Stark apparatus was implemented to remove this water. After about 2 hours of reaction, toluene was removed from reaction medium and creation of bisphenolate was completed. Then, reaction temperature was increased to about 180°C to production of polymer in 4-6 hours. This reaction is an aromatic nucleophilic substitution reaction. Since, aromatic nucleophilic substitution reaction needs the presence of a strong nucleophilic group, [33] K_2CO_3 was used in order to convert bisphenol to the strong nucleophilic component of bisphenolate [34]. The reaction led to production of the ether, is named as Williamson synthesis [33]. Nucleophilic substitution

of aryl halides is rather hard to occur; however, presence of C=O group in para and Ortho position relative to halogen, leads to easy reaction of these components [33]. Intrinsic viscosity of synthesized PAEKs was measured by preparation of a 0.1% w/v solution of these polymers in dimethylacetamide. The measured intrinsic viscosities of all the synthesized polymers were in the range of 0.33-0.54 dl/gr. Furthermore, the structure of synthesized polymers was analyzed and confirmed by FTIR and NMR spectroscopy techniques. Disappearance of -OH and C-F peaks in the ranges of 3500-3650 and 1263 cm⁻¹, respectively, confirms the production of polymer. Also, stretching absorption peak of C-O-C at 1229 cm⁻¹ affirms the formation of etheric bonds. In ¹H NMR spectra, signals of 1.34, 4.5 and 7.2-8.7 ppm associate with CH₃, CH₂ and protons of aromatic groups, respectively.

Viscosity and molecular weight calculations

Viscosity measurement with the purpose of molecular weight determination of synthesized PAEKs was performed using an

	DMAC	P1			P2			P3		
Concentration (g/dl)	-	0.1	0.2	0.5	0.1	0.2	0.5	0.1	0.2	0.5
Passing time (s)	17.34	17.91	18.01	18.23	18.28	18.47	19.15	17.99	18.08	18.36
η _{inh} (dl/g)	-	0.32	0.18	0.1	0.53	0.31	0.19	0.36	0.2	0.11
η _{intrinsic} (dl/g)	-	0.33			0.54			0.37		
Molecular weight	-	14900			31800			17750		

Table 1: Inherent viscosity, intrinsic viscosity and molecular weight of synthesized PAEKs.

Finally, using Mark-Houwink equation (Equation 2) and setting a and b constants for PAEK equal to 6.4×10^{-4} and 0.65 [35], respectively, the molecular weights of synthesized polymers were calculated. As it is seen in Table 1, molecular weight of P2 is higher than other polymers.

$$[\eta]_{\text{PAEK}} = 6.4 \times 10^{-4} M^{0.65} \text{ (Equation 2)}$$

Solubility properties

Conventional PAEKs without side groups could not be dissolved in most known organic solvents [36] while, as it is seen in Table 2, the

	DMSO	NMP	DMF	THF	DMAC	DCM	H ₂ SO ₄	CHCl ₃	MeOH	EtOH	Acetone
P1	+	+	+	+	+	-	+	±	-	-	-
P2	±	+	±	±	+	-	+	±	-	-	-
P3	+	+	+	+	+	-	+	±	-	-	-

Note: '+' is soluble, '-' is insoluble with heating, '±' is soluble with heating

Table 2: Solubility properties of synthesized PAEKs.

Thermal properties

TGA thermograms of synthesized polymers have been demonstrated in Figure 3 and the values of T5, T10, T25 and T50, corresponding to weight losses of 5%, 10%, 25% and 50%, respectively,

Ubbelohde viscometer. Solutions of synthesized polymers in DMAc solvent at the room temperature of 25°C and at 3 different concentrations of polymers were prepared. Then the passing time of prepared solutions between two signs of viscometer (t) along with the passing time for pure solvent (t₀) were recorded and tabulated in Table 1. Using the following equation (Equation 1) inherent viscosity for each sample was calculated.

$$\eta_{\text{inh}} = \ln(t/t_0)/C \text{ (Equation 1)}$$

Where, C=concentration

Also, by extrapolation of the inherent viscosity values to the zero concentration of polymer, intrinsic viscosity values were achieved (Table 1).

novel synthesized PAEKs are soluble or partially soluble in the most aprotic polar (DMF, DMAc, NMP, THF, DMSO, etc.) solvents and also in the concentrated sulfuric acid (H₂SO₄). It is well known that the introduction of flexible alkyl side chain attached to Nitrogen atom of the bisfluoro monomer has a positive effect on the polymer solubility; while, this effect is reduced in bisphenol containing two aromatic fused rings. In the present case, it is seen that P2 consisting of bisphenol 1, 5-naphthalenediol monomer, owns less solubility in comparison with P1 and P3. In addition, the presence of 3, 6-disubstituted carbazole induces a bent conformation for polymer chain with benefits on polymer solubility [37,38].

and also residual weight (R_w) at 600°C all have been tabulated in Table 3.

	T _{5%} (°C)	T _{10%} (°C)	T _{25%} (°C)	T _{50%} (°C)	R _w (wt. %)
P1	364	413	522.21	580.37	24.5

P2	332	432	554.76	597.13	47.92
P3	352	426	518.14	593.5	43.5

Table 3: Thermal stability parameters extracted from TGA thermograms.

It is seen in Figure 3 that there are three min mass loss steps in degradation process of all the PAEKs. The first small weight loss ranged from 110°C to 180°C can be attributed to the loss of residual moisture and solvent. The second step, starting at about 350-370°C attributes to the degradation of the alkyl group attached to the Nitrogen atom or could be due to the decomposition of the oligomers at lower temperatures or the reaction between the terminal hydroxyl and terminal fluorine groups at relatively high temperatures [38]. The third weight loss step started at around 530°C, 560°C and 550°C for P1, P2 and P3, respectively can be ascribed to the decomposition of the polymer backbone. Furthermore, the char yields at 600°C are 47.92% for P2, 43.5% for P3 and 24.5% in the case of P1. Therefore, it can be concluded that generally P2 possesses the best thermal stability among these synthesized PAEKs. Differences in thermal performance of polymers can be explained based on differences in chemical structure of monomers. P2, because of having two aromatic fused rings has more potential to sustain against temperature raise and its ability in char formation is more than P1 and P3. Also, the differences in the case of P1 and P3 can be attributed to the position of bonds on repeating unit of polymer, i.e., para or meta.

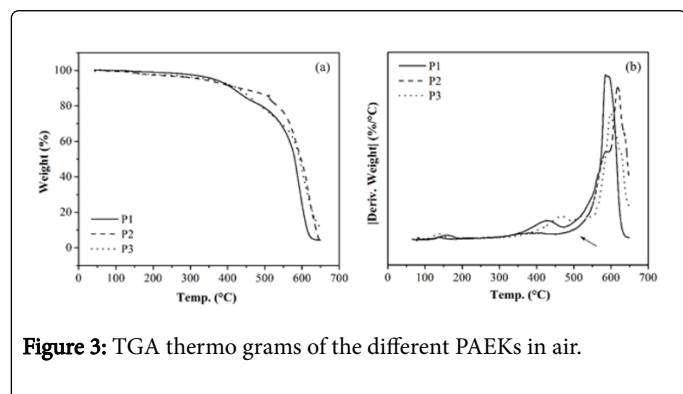


Figure 3: TGA thermo grams of the different PAEKs in air.

The DSC curves of synthesized polymers are depicted in Figure 4. In all the samples a small endothermic peak is recognized at around 100°C which attribute to the relaxation process of polymer segments. Glass transition temperatures (T_g) of these polymers were determined equal to 105, 88 and 125°C for P1, P2 and P3, respectively. Furthermore, the presence of no melting endotherms in the DSC thermo gram is an indicative of amorphous nature of synthesized PAEKs. The exothermic peak which is seen in the case of P2 relates to some processes similar to cold crystallization phenomenon. In P2, since the molecular structure of repeating unit is more rigid than P1 and P3 therefore in the cooling cycle these chains do not have enough time to enter into more ordered phases, while during heating they enter to order structures and hence show exothermic peak. It should be noted that as mentioned earlier all the three polymers have no melting peaks therefore the exothermic peak of P2 can be not attributed to the cold crystallization and it only relates to some exothermic transitions originating from some enhancement in extent ordered structures.

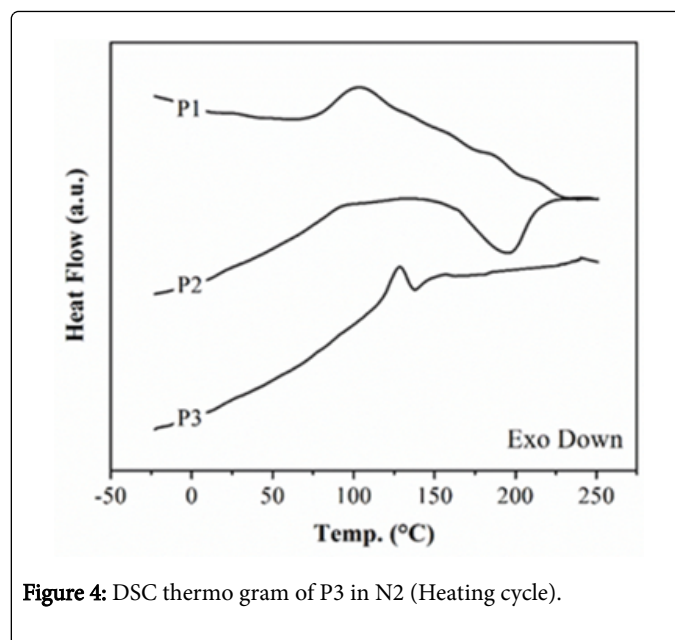


Figure 4: DSC thermo gram of P3 in N2 (Heating cycle).

Conclusion

A novel series of PAEKs containing 9-ethylcarbazole groups in their main chain were synthesized by reaction between three different bisphenols with the produced new difluoride monomer. The formation of PAEKs was confirmed using spectroscopic techniques of FTIR and ¹HNMR. Later on, the properties of synthesized PAEKs were analyzed in terms of solubility, viscosity and thermal properties. The inherent viscosities of PAEKs were estimated in the range of 0.32-0.53 dl/g for solutions of 0.1 g/dl in DMAc at 25°C. It was indicated that all the synthesized PAEKs unlike the conventional PAEKs, were soluble or partially soluble in the common aprotic organic solvents such as DMAc, NMP, DMF and DMSO and also in concentrated H₂SO₄. TGA traces of the novel PAEKs showed a minor mass loss of about 10 wt. % until 400°C which is an indication of considerably high thermal stability of these polymers. By comparing mass loss values of these polymers at same temperatures and also considering their char yield at 600°C, it was concluded that P2 possesses the best thermal stability among the all novel PAEKs. Higher glass transition was determined to P3 in DSC experiment. Differences in thermal properties including glass transition and thermal stability of polymers were explained based on structural differences of monomers and their para/metapositional isomerism. Moreover, results of DSC experiment showed that there are no crystalline structures in the synthesized PAEKs.

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