

# Synthesis and Thermal Properties of Poly (aryl ether ketone)s Containing Dibenzoylbiphenyl Moieties Copolymers

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## Abstract

Poly (ether biphenyl ether ketone) (PEDEK)-poly (ether biphenyl ether ketone biphenyl ketone) (PEDEKDK) copolymers were prepared by nucleophilic substitution routes. Transformational behavior of  $T_g$  and  $T_m$  for PEDEK-PEDEKDK copolymers with various  $n_B$  was studied by using DSC. Results revealed that the glass transition temperature  $T_g$  for the copolymers evidently increased as the content of PEDEKDK units increases. The melting points ( $T_m$ ) of the copolymers obviously depended on  $n_B$  and showed the behavior of eutectic type copolymer. Isothermally crystallized PEDEK-PEDEKDK copolymer ( $n_B=0.7$ ) exhibit a novel double-melting behavior i.e. the high-melting peak temperature changed with the increasing of annealing temperature or time at higher annealing temperature.

**Keywords:** Poly(aryl ether ketone), copolymer, transformation of  $T_g$  and  $T_m$ , DSC

## Introduction

Aromatic poly (ether ketone) are an important class of grind resistance and radiation resistance high-performance engineering thermoplastic, which have good thermal stability, great mechanical stability. The most well known sample is poly (ether ether ketone) (PEEK) which is semicrystalline material. However its a relatively low glass transition temperature( $T_g$ ) of 145°C and  $T_m$  of 334°C limit PEEK widespread application. In order to increase using temperature of material, synthesis of structurally related polymers which have higher  $T_g$ s, has been considered interest. Therefore, structure-property relationships in PEEK systems also have been extensively investigated as a main subject for practical applications. It has been proved that increase benzoyl contents or carbonyl to ether ratios in poly (aryl ether ketone)s lead to stiffer polymer backbones, giving higher  $T_g$ s and melting points as PEEKK. Another modification to improve its resistance, replacement of its phenylene moiety to biphenylene moiety has been proved to be effective.

Multiple melting peaks have been observed in Poly(aryl ether ketone)s of homopolymers and copolymers. It is known that upon crystallization or annealing of PAEKs at a given temperature and for a given time, the melting scan exhibits two endothermic peaks. The characteristics of the lower endothermic known from the literature<sup>(1-5)</sup> are: 1) The low-melting peak temperature is independent of poly(aryl ether ketone) composition and melting point ( $T_m$ ) and is related to

crystallization temperature, time and heating rate. 2) It appears 10-15°C above the annealing (or crystallization) temperature i.e. peak shifts up with increasing the annealing or crystallization temperature when the crystallization temperature is high enough ( $T_m - T_c < 20^\circ\text{C}$ ) only one melting peak appears at about  $T_m$ ; 3) Peak shifts up in temperature with increasing of the crystallization or annealing time at given temperature. When crystallization temperature is high enough ( $T_m - T_c < 20^\circ\text{C}$ ), the low melting peak disappears with prolonging crystallization. The high-melting peak is independent of crystallization temperature, time and heating rate.

Our studies have focused on the insertion of both keto- and biphenyl groups in the repeat unit of poly (aryl ether ketone)s. So we have prepared monomer 4,4'-bis(4-fluorobenzoyl)biphenyl, then prepared a series of polymers which contains PEDEK, PEDEKDK and PEDEK-PEDEKDK copolymers (see scheme 1). The thermal properties and melting behavior of these polymers were studied by DSC. In these studies, we found a new phenomenon in the causing of heating treatment PEDEK-PEDEKDK copolymer i.e. the high-melting peak temperature changed with the increasing of annealing temperature or time at higher annealing temperature and the low-melting peak temperature disappeared.

## Experimental

### *Monomer Synthesis*

#### 4-chloro-4'-fluorobenzophenone

4-chloro-4'-fluorobenzophenone was synthesized using an identical procedure to that described for 1. A 3L three-neck, round-bottomed flask equipped with mechanical stirrer and dropping funnel and a thermometer were placed fluorobenzene (2000ml) and Aluminum chloride (400g). o-chlorobenzoyl chloride(250ml) was then added to the reaction mixture. The reaction was stirred at 50-60°C for 3h. The solvent was evaporated and the product was collected by filtration, dried and recrystallized from Ethel affording 350g (85%) of white crystal. M.p.116-118°C. <sup>1</sup>H-NMR (400MHz,

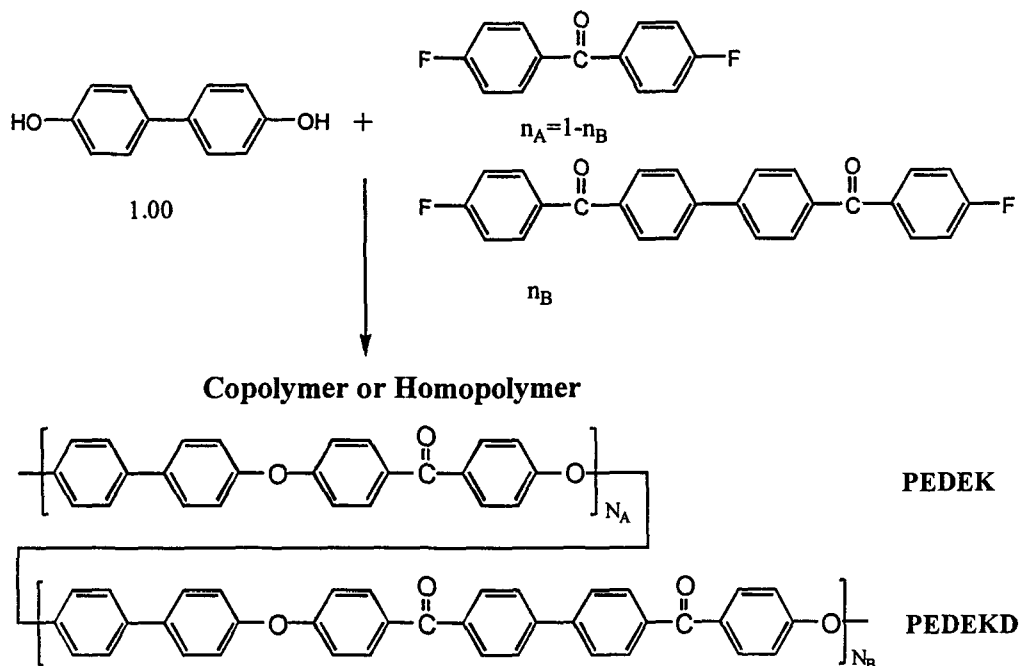
#### 4,4'-Bis(fluorobenzoyl) biphenyl

A 2L three-necked, round-bottomed flask equipped with mechanical stirred was charged with nicked bromide (10g), Pph<sub>3</sub>(90g) zinc dust (90g). DMAC (500ml) was then added to the reaction mixture as a solvent. The temperature was increased to 50°C to generate the red Ni(PPh<sub>3</sub>)<sub>4</sub> catalyst. 4-chloro-4'-fluorobenzophenone(212g 0.9mol) was added to the mixture through the solid addition funnel. The green-brown mixture was heated further 90°C and stirred 1h. The crude product was obtained. Recrystallization from DMF gave the final product. Yield: 150g (85%) m.p. 268°C. <sup>1</sup>H-NMR MS

### *Polymer Synthesis*

Polymer was synthesized by nucleophilic substitution reaction of difluoromonomer with 4,4'-

biphenol using diphenylsulfone as a solvent. The reaction was heated to 320°C by  $K_2CO_3$  and  $Na_2CO_3$  as a base for 5h. The solution was poured into water and precipitate was obtained. After the crude polymer was crushed filtered, washed and dried, a powder resin was finally obtained.



### Methods

The powder resin, wrapped aluminum foil, was molded on a compression machine at a fixed temperature. The molded film was quenched into water as quickly as possible to obtain an amorphous sheet. Dupont TA-910 differential scanning calorimetry (DSC) was carried out at a heating rate of 20°C/min from 100°C to 500°C under nitrogen atmosphere, and at least 10mg of the film a sample used for DSC measurement.

MS, NMR, WAXD

## Results and Discussion

### PEDEK and Its Random Copolymers

The synthesis of PEDEKDK was achieved by nucleophilic substitution reaction of 1a with 4,4'-biphenol in the presence of a mixture of alkali metal carbonate using diphenylsulfone as a solvent. As a poor solubility of the polymer, PEDEKDK was obtained inherent viscosities of 0.6dl/g. The materials obtained could not be molded into tough sheet.

A series of copolymers were prepared in a similar manner by 2a with 4,4'-biphenol. All polymers gave intrinsic viscosities above 0.78dl/g measured in concentrated sulfuric acid, which is indicative of a high molecular weight for these copolymers. All measured thermal properties for copolymers are summarized in Table 1.

The difference in chemical structure between PEDEK and PEDEKDK is that PEDEKDK in group between two ether groups. Because biphenyl ketone groups are inserted, the molecular

chain rigidity is increased. The PEDEK homopolymer has a  $T_g$  at 171°C,  $T_m$  at 409°C. The PEDEKDK homopolymer has a  $T_g$  at 210°C,  $T_m$  at 467°C. The DSC curves of the amorphous copolymers are shown in Figure 1. Each copolymer exhibits only a single glass, which was almost not broadened. Results revealed that  $T_g$  values for the copolymers are shifted gradually to higher temperature when compared with that of PEDEK, and increase as the PEDEKDK content increase.

The  $T_g$  of copolymer follow the Fox equation:  $1/T_g = W_A/T_{gA} + W_B/T_{gB}$ , where  $T_g$ ,  $T_{gA}$ ,  $T_{gB}$  are the glass transition temperatures of copolymer, PEDEK and PEDEKDK, respectively.  $W_A$  and  $W_B$  are the weight fraction of PEDEK and PEDEKDK, respectively. In Fig.2, the experimental  $T_g$  of copolymer is in agreement with calculated value from the Fox equation. □ All copolymer have  $T_g$  values well above that of PEEK, indicating that the extra keto- and biphenyl groups cause an increase in the polarity and the rigidity in the polymer chain.

The plots of  $T_m$  values vs weight fraction of PEDEKDK unit ( $n_B$ ) of the copolymers are shown in Fig. 3. As is obvious from Fig 3, it is found that the PEDEK-PEDEKDK copolymer belongs to a eutectic type and the melting temperature assumes a minimum values. It is well known that  $T_m$  of polymer is thermodynamically expressed by Eq:  $T_m = H/S$ . When the PEDEKDK unit is introduced,  $S$  increases because of the destruction of regularity of the molecular chain, that is,  $T_m$  decreases. On the contrary, as the content of the PEDEKDK segment increases,  $H$  increases because the rigidity of the molecular chain is strengthened so that  $T_m$  increases at  $n_B=0.35$  or above. When  $n_B=0.4$ ,  $T_m$  exhibit a special appearance which shows multi-peaks. This phenomenon appeared in the other copolymer systems under similar circumstance.

#### ***Melting behavior of isothermally crystallized PEDEK-PEDEKDK copolymer ( $n_B=0.7$ )***

Blundell<sup>(7)</sup> first reported the double-melting phenomenon for PEEK crystallized in the range of temperature. The other poly(aryl ether ketone)s (PAEKs), such as PEK, PEEK, PEDEK<sup>(5)</sup>, PEDEKK<sup>(6)</sup>, etc., also exhibit this behavior. Therefore the double-melting behavior is characteristic of the PAEKs family. The copolymer what we have prepared exhibits its  $T_g$  and  $T_m$  at 192°C and 414°C measured by DSC, which is expected to use at above 300°C. Therefore, the investigation of relationship between structure and thermal properties of the material has a great value for the materials application.

**Dependence of the melting peaks on crystallization temperature.** Fig 1 shows the curves of PEDEK-PEDEKDK copolymer ( $n_B=0.7$ ) film crystallized from the glassy state at different temperatures. The copolymer also exhibited the double-melting behavior in the lower annealing temperature. The low-melting peak temperature was at about 20°C above the crystallization temperature. When the annealing temperature was above 310°C, the low-melting peak disappeared and the high-melting peak temperature also changed. Both the variation of the low- and high-melting peak temperature showed in Table 1. We can see that  $T_{m2}$  remained unchangeable when annealing temperature  $T_c$  was lower than 250°C. When  $T_c$  was higher than 310°C,  $T_{m1}$

disappeared and Tm2 shifted to the lower temperature. When the copolymer was annealed at between 310°C and 340°C, Tm2 shifted from 414°C to 388°C, the melting peak exhibited a sharp peak. The relationship of annealing temperature with low- and high-melting peak temperature was plotted in Fig2.

**Dependence of the melting temperature on crystallization time.** From Fig 1, we have obtained that melting behavior of the copolymer from the glassy state isothermally crystallized at 250°C and 340°C is different. Therefore we annealed the film isothermally crystallized at 250°C and 340°C in different crystallization time, respectively.

Fig 3A shows the DSC curve of film crystallized at 250°C for the different crystallization time. The high-melting peak temperature was maintained at about 414°C while the low-melting peak temperature increased gradually with the increasing crystallization time until it reached a stable value. The low- and high-melting peak temperature of the copolymer film annealing at 250°C were plotted vs. crystallization time shown in Fig 4. But the DSC curve of film crystallized at 340°C for the different crystallized time exhibited different results (see Fig3B). The low-melting peak exists only in the shorter time. When time is above 20min, the low-melting peak disappears, the high-melting peak temperature shifts to the lower temperature gradually (from 414°C to 388°C) with the increasing of the crystallization time up to a stable value after 60min. Detailed data on the copolymer was annealed at 340°C in different time was listed in table 2. The low- and high-melting peak temperature were plotted vs. Crystallization time shown in Fig 5. In Fig4 and Fig 5, we can see that the results of the copolymer be annealed at 340°C and 250°C in different time has obviously different with the other PAEKs.

## Conclusions

We have obtained the following results for PEDEK-PEDEKDK isothermally crystallized from the glassy state:

1. The high-melting peak is dependent of crystallization temperature. The high-melting peak temperature shifts gradually with the increasing of the crystallization temperature.
2. The high-melting peak is dependent of crystallization time at some a given temperature, i.e. the high-melting peak temperature shifts with the increasing of crystallization time at higher annealing temperature and remains unchangeable at lower annealing temperature.

## Acknowledgments

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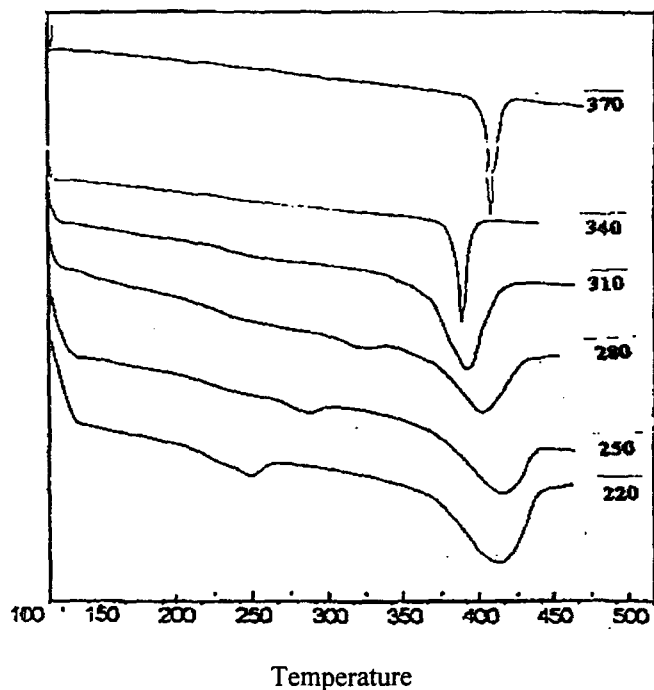


Fig 1 DSC traces of the copolymer film crystallized from the glassy state at different heating treatment temperatures for 5h .

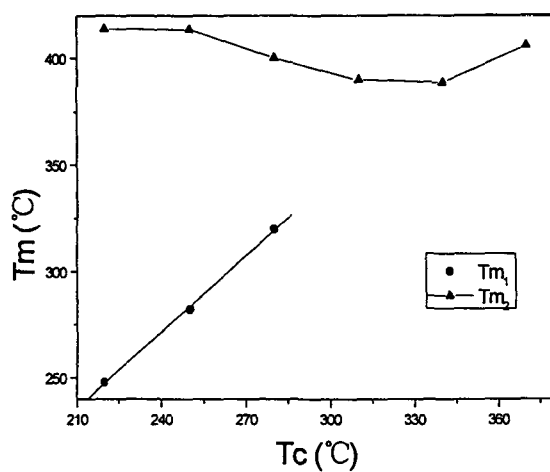


Fig 2 Variation of the low- and high-melting peak temperatures with crystallization temperature

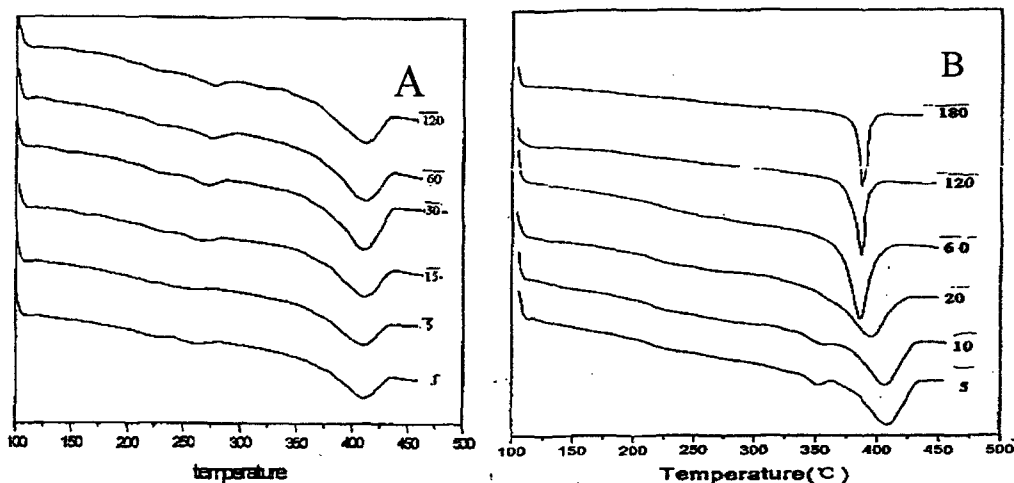


Fig 3 DSC traces of the copolymer film crystallized from the glassy state at 250°C(A) and 340°C (B) for different

Table 1 Data of Annealing the Copolymer in Different Temperature for 5h

Tc (°C)	220	250	280	310	340	370
Tm1 (°C)	248	282	322	—	—	—
Tm2 (°C)	413	413	401	390	388	409

□

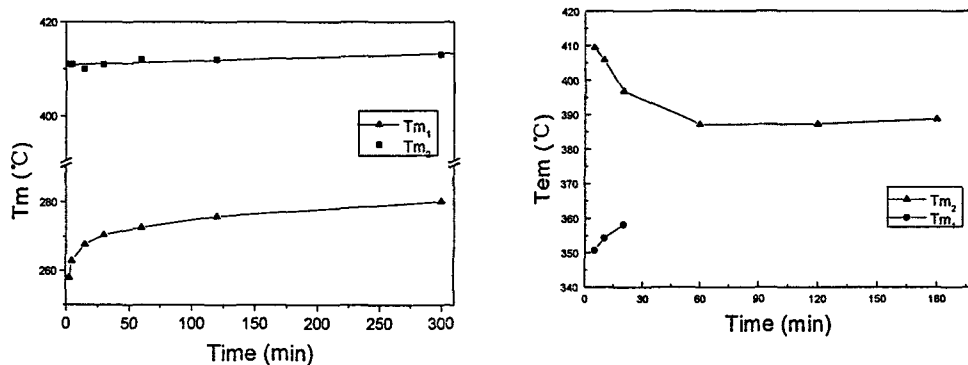


Fig 4 Variation of the low- and high-melting peak temperatures with crystallization time at 250°C

Fig5 Variation of the low- and high-melting peak temperatures with crystallization time at 340°C

Table 2 Data of Annealing at 340°C in Different Crystallized Time

T(min)	5	10	20	60	120	180
Tm' (°C)	350.7	354.3	360			
Tm (°C)	409	405.7	396.7	387	387.1	388.2