

Notes

**SYNTHESIS AND CHARACTERIZATION OF
POLY(ARYL ETHER KETONE) FROM 4-(3-PHENYL-4-
HYDROXYPHENYL)PHTHALAZINONE***

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Abstract A novel soluble poly(aryl ether ketone) was prepared by the reaction of 4-(3-phenyl-4-hydroxyphenyl)phthalazinone with 4,4'-difluorobenzophenone. The polymer was characterized by DSC, TGA and X-ray diffraction.

Keywords Poly(aryl ether ketone), Synthesis, Heterocyclic polymer

INTRODUCTION

Poly(aryl ether ketones) have received commercial interest because of their high mechanical and thermal stability and fire retardance^[1~3]. The synthesis of these materials is usually performed by Friedel-Crafts acylation or by nucleophilic aromatic displacements. Heterocyclic poly(aryl ether ketone) from 4-(4-hydroxyphenyl)phthalazine-1-one has been prepared^[4]. This polymer is a high performance thermoplastics and has high glass transition temperature (263°C). In the present paper the synthesis of a new type of soluble poly(aryl ether ketones), (PPEK), starting from 4-(3-phenyl-4-hydroxyphenyl)phthalazine-1-one was described.

EXPERIMENTAL

Monomer Synthesis

The new bisphenol monomer 4-(3-phenyl-4-hydroxyphenyl) phthalazine-1-one was synthesized according to Ref. [5]. It was purified by recrystallization from ethanol to give high purity monomer, m.p. 292°C; IR (cm⁻¹): 3293 (s, NH and OH), 3205 (w, Ar-H), 3093 (w, Ar-H), 1644 (s, C=O), 1610 (m, C=N and C=C of Ar), 1586 (m), 1480 (m), 1202 (s), 842 (s), 777 (s); ¹H-NMR (δ): 12.6 (s, 1H, NH), 9.7 (s, 1H, NH), 8.2~8.5 (m, 1H, 8-H).

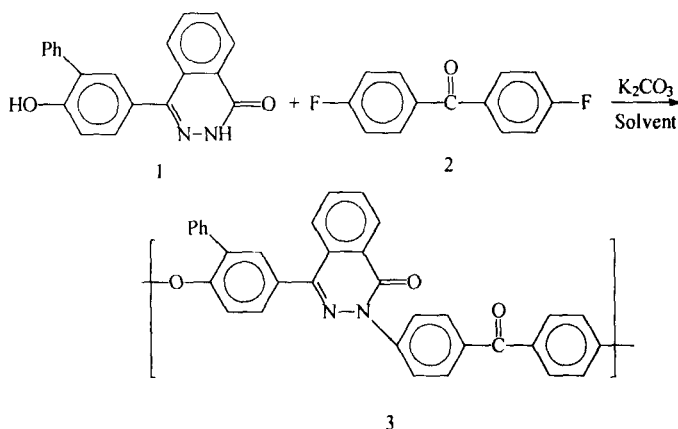
Polymer Synthesis

In the presence of anhydrous potassium carbonate, PPEK was prepared in solvent by the nucleophilic condensation of 4-(3-phenyl-4-hydroxyphenyl) phthalazine-1-one with 4,4'-difluorobenzophenone under N₂ atmosphere as shown in Scheme 1. The reaction mixture was stirred at 140~230°C for 4~18 h. After cooling, the reaction mixture was poured into hot water to precipitate the PPEK, which was reprecipitated from CHCl₃/ethanol to produce white products and was then dried in a vacuum oven at 80°C.

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Scheme 1

RESULTS AND DISCUSSION

The structure of the phthalazinone monomer was confirmed by FT-IR and $^1\text{H-NMR}$ data. The monomer, recrystallized from ethanol as a white crystalline solid, could react with 4,4'-difluorobenzophenone to give the polymer. All reactants were mixed in solvent and then heated at $140\text{--}230^\circ\text{C}$. High molecular weight polymer was readily formed in 4~18 h. A few hours are needed to remove water azeotropically prior to polymerization in order to get a polymer with high molecular weight. The η_{inh} was determined in CHCl_3 at 25°C and found to be 0.70 (dL/g) .

The FT-IR spectrum of the polymer (Fig. 1) shows a strong peak of carbonyl group absorption at 1670 cm^{-1} . The peaks at 1598 , 1499 , 1449 and 1414 cm^{-1} belong to the absorption of phenyl groups, while the peak at 1234 cm^{-1} is due to the C-O-C bond absorption. The spectrum of polymer does not exhibit a broad absorption band at $3200\text{--}3500\text{ cm}^{-1}$ which could be assigned as the stretching vibration of $-\text{OH}$ and $-\text{NH}$ groups in the monomer. This implies that the reaction did occur as we expected.

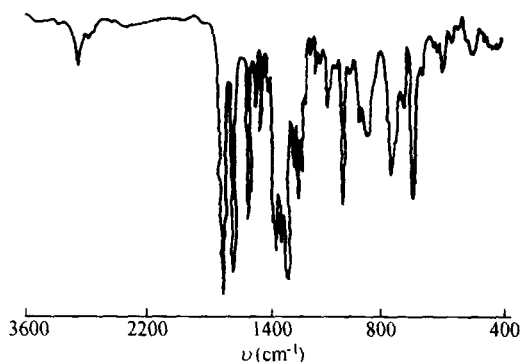


Fig. 1 The FT-IR spectrum of the polymer

The thermogram obtained from differential scanning calorimetry analysis was depicted in Fig. 2. It shows that the polymer has a high glass transition temperature (250°C). Thermo-gravimetric analysis (Fig. 3) shows that the polymer has good thermooxidative stability with 5% weight loss around 480°C under an atmosphere of air due to the presence of the phthalazinone moiety. The polymer was proved to be an amorphous one by X-ray diffraction analysis.

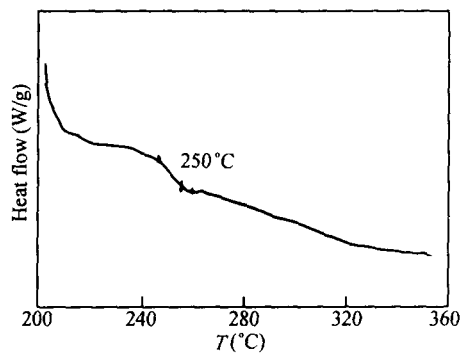


Fig. 2 DSC analysis of the polymer

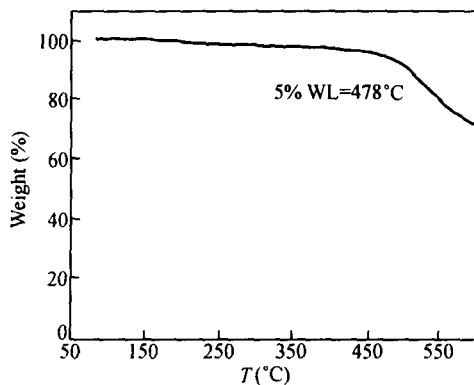


Fig. 3 TGA curve of the polymer

The polymer is soluble in most chlorinated solvents such as chloroform, tetrachloroethane as well as in NMP, DMAc, DMF etc. The phenyl groups on the stiff polymer chains lead to an increase in its solubility.

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