

Notes

SYNTHESIS AND CHARACTERIZATION OF POLY(ARYL ETHER KETONE) CONTAINING BIPHENYLPHthalAZINONE MOIETY*

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Abstract A new poly(aryl ether ketone) containing biphenylphthalazinone moiety was prepared by the reaction of 4-(4-hydroxybiphenyl) phthalazine-1-one with 4, 4'-difluorobenzophenone. The monomer and the polymer were characterized by FT-IR and ¹H-NMR. Some properties of this polymer were described.

Keywords Poly(aryl ether ketone), Biphenylphthalazinone

INTRODUCTION

Since poly(ether ether ketone) (PEEK) has been shown to be promising as an excellent engineering plastics due to its good mechanical properties and thermooxidative stability, the synthesis of aromatic poly(ether ketone)s has become of interest in recent years^[1-3]. They have found many applications in the electronics and aerospace industries. Recently, we reported the synthesis of a new poly(ether ketone) which was prepared from hydroxyphenylphthalazinone. It has good mechanical properties and thermooxidative stability^[4-5]. This paper describes the successful synthesis of a new poly(aryl ether ketone).

EXPERIMENTAL

Monomer Synthesis

The new bisphenol monomer 4-(4-hydroxybiphenyl) phthalazine-1-one was synthesized according to Ref. [5]. It was purified by recrystallization from ethanol to give high purity monomer, m.p. 335°C; IR (cm⁻¹): 3280 (*s*, NH and OH), 3149~3020 (*ms*, Ar-H), 1648 (*s*, C=O), 1607 (*s*, C=C and C=N) 1589,1462 (*s*, C=C of Ar), 1268 (*ms*), 1209 (*ms*), 1193 (*ms*), 1175 (*ms*), 824 (*s*) and 799 (*ms*), ¹H-NMR (δ): 12.63 (*s*, 1H, NH), 9.31 (*s*, 1H, NH) and 8.36 (*m*, 1H, 8-H); Elemental anal: Calcd. for C₂₀H₁₄O₂N₂(%): C 76.43, H 4.46, N 8.92; Found(%): C 76.43, H 4.63, N 9.13.

Polymer Synthesis

The scheme shows the preparation process of the heterocyclic polymer. In the presence of the anhydrous K₂CO₃, the polymer was prepared by the nucleophilic condensation of the phthalazinone monomer and 4,4'-difluorobenzophenone under N₂ atmosphere. In order to get a polymer of high molecular weight, a few hours are needed to remove water azeotropically prior to polymerization. After reaction, the reaction mixture was poured into ethanol to precipitate a white polymer which

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was washed with water. The solid product was purified by dissolving in CHCl_3 and reprecipitating in ethanol. The white fibrous polymer was filtered and dried in a vacuum oven at 80°C . Inherent viscosity was measured in CHCl_3 at $25 \pm 0.1^\circ\text{C}$.

RESULTS AND DISCUSSION

A high molecular weight polymer with inherent viscosity 0.70 dL/g was obtained. The NH group of the phthalazinone moiety can form N^+K^+ , which is capable of nucleophilic condensation.

FT-IR spectra of the monomer and the polymer are shown in Fig. 1a) and Fig. 1b), respectively. The spectrum of monomer shows strong carbonyl group absorption at 1671 cm^{-1} . The peaks at 1592, 1495, 1450 and 1411 cm^{-1} are the absorption of phenyl groups. By comparing spectrum a) with b), we find that the broad peak at $3200\sim 3500\text{ cm}^{-1}$ in a) is due to the OH group and NH group absorption of the monomer which is absent in b). And the new peak at 1243 cm^{-1} in b) can be assigned to the C—O—C absorption of the polymer which is absent in a). This implies that the reaction has taken place as expected. The ^1H -NMR spectra of the monomer and the polymer are shown in Fig. 2a) and Fig. 2b), respectively. From spectrum b), we could not find the protonic OH and NH signals which existed in a). The ^1H -NMR spectra also verify the reaction.

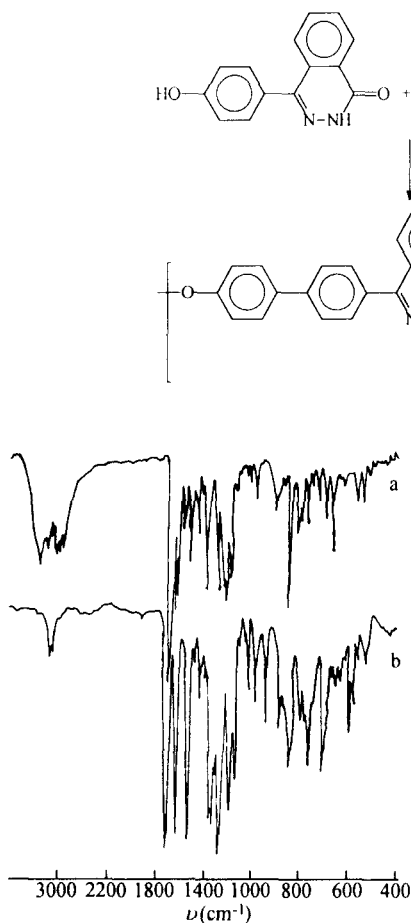


Fig. 1 The IR spectra of the monomer a) and the polymer b)

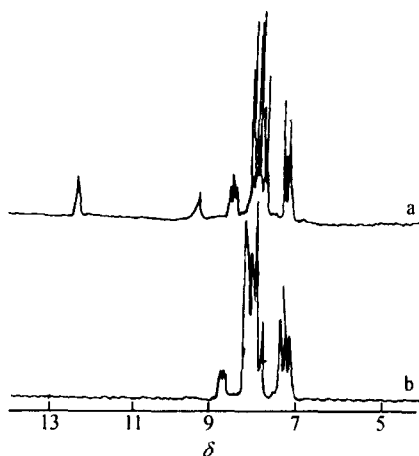


Fig. 2 The ^1H -NMR spectra of the monomer a) and the polymer b)

The results of differential scanning calorimetry analysis and the thermogravimetric analysis

of the polymer are shown in Fig. 3. This indicates that the polymer has high thermostability. The glass transition temperature was found to be 288°C, about 35°C higher than the polymer from 4-(4-hydroxyphenyl)phthalazine-1-one. This could be explained by the introduction of the biphenyl group into the polymer. The polymer exhibits good thermal stability with no weight loss below 400°C.

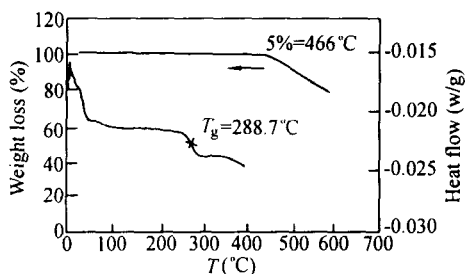


Fig. 3 The results of DSC and the TGA of the polymer

This polymer is soluble in several organic solvents such as CHCl_3 , DMAc, NMP, etc. and could be cast from solution to form mechanically strong films. The good solubility could be attributed to the introduction of the phthalazinone moiety. Further work is in progress.

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