

Synthesis and Properties of Polyetherketones Containing Sulfide and Phthalazinone

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Abstract: High molecular weight copoly(ether ketone)s (PEK) based on 4-(4-hydroxyphenyl)-1-phthalazinone (DHPZ)/4,4'-thiobisphenol (TBP)/4,4'-difluorodiphenylketone (DFK) were prepared by nucleophilic substitution polycondensation. The copolymers were characterized by FT-IR and ¹H-NMR. Thermal properties and solubility of copolymers were studied.

Keywords: Polyetherketones, 4,4'-thiobisphenol, 4-(4-hydroxyphenyl)-1-phthalazinone.

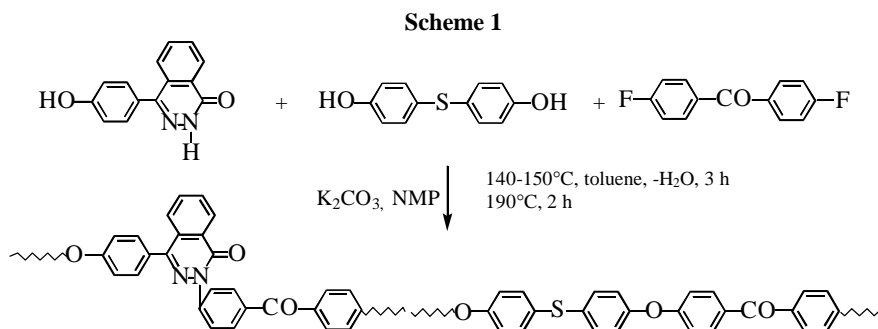
Polyarylethers containing phthalazinone are high performance engineering plastics that give rise to much interest in applications as high temperature resistant materials¹⁻³. Poly(phthalazinone ether ketone) (PPEK) has a high glass transition temperature ($T_g=263^\circ\text{C}$) and excellent solubility in many common polar organic solvents such as chloroalkane, which is very different from most of poly(aryl ether ketone)s. However, its bad melting processability limits its application⁴. In the present study, we aim to improve the properties of PPEK through copolymerization.

The PEKs containing phthalazinone and sulfide were prepared by the reaction of 4,4'-thiobisphenol (TBP) and 4-(4-hydroxyphenyl)-1-phthalazinone (DHPZ) with 4,4'-difluorodiphenylketone in the presence of potassium carbonate and N-methyl-2-pyrrolidone (NMP). The synthesis procedure was outlined as follows (**Scheme 1**). After refluxing in toluene at 140-150°C for 2-3 h, the temperature was raised to 190°C to polymerize for 3 h. The viscosities of polymers in CHCl_3 at 25°C were more than 0.51 dL/g. The polycondensation procedure showed that sulfolane was not a suitable reaction medium for the synthesis of PEK. When the feed ratio of the TBP component more than 20%, the crosslinked polymers formed in sulfolane. Similar phenomena had been found in synthesis of polymers containing sulfur and the detailed explanations were given in some literatures⁵⁻⁶.

The structures of the copolymers were characterized by spectroscopic means. No characteristic absorption of phenols at 3300 cm^{-1} was found in the FT-IR spectra of the copolymers and the absorption at 1090 cm^{-1} indicated that the copolymers containing sulfide. In the ¹H-NMR spectra of the copolymers, the signal at about 7.33 ppm was peculiar to the protons of phenyl groups adjacent to sulfide and the signal at about 8.57

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ppm to the proton near to C=O of *endo*-amide bond of phthalazinone. Their intensity ratios were similar to the feed molar ratios of TBP and DHPZ. All of these data showed agreement with the proposed structure.



The results of differential scanning calorimetry (DSC) indicated that each copolymer containing a certain ratios of TBP or DHPZ had only one glass transition temperature (T_g) in the range of 137°C to 263°C, and T_g increased linearly with the increase of the molar fraction of DHPZ. The results demonstrated that the copolymers were random and homogeneous. Thermogravimetric analysis showed that the initial degradation temperatures of the copolymers were similar to that of PPEK at about 470°C. The copolymers containing more DHPZ component had better solubility in some aprotic polar solvent, such as NMP, N, N'-dimethylformamide (DMF), N, N'-dimethylacetamide (DMAc) and chloroalkane. When TBP contents were more than 30%, the copolymers were not soluble in some aprotic polar organic solvents, such as sulfolane, DMAc, DMF, and had better solubility in an aprotic dipolar organic solvents, such as NMP.

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