

## Synthesis of Poly(phthalazinone ether ketone) Containing Sodium Sulfonate Groups *via* Direct Polymerization

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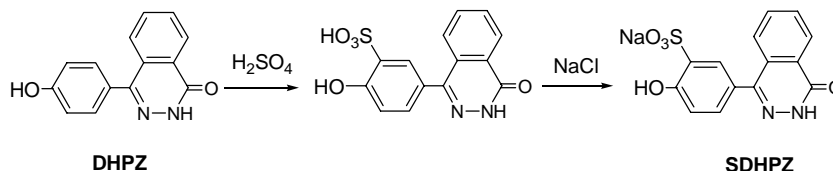
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**Abstract:** 1, 2-Dihydro-4-(4-hydroxyphenyl)(2H)phthalazin-1-one(DHPZ) was sulfonated in concentrated sulfuric acid. Poly(phthalazinone ether ketone) containing pendant sodium sulfonate group was synthesized from sulfonated and pure 1,2-dihydro-4-(4-hydroxyphenyl)(2H)phthalazin-1-one, and 4,4'-difluorodiphenylketone. The sulfonated monomer and sulfonated polymer were characterized with FT-IR and  $^1\text{H-NMR}$ .

**Keywords:** Sulfonation, synthesis, poly(phthalazinone ether ketone).

Poly (aryl ether ketone)s are a category of high performance engineering plastics which have outstanding thermal, physical and mechanical properties. Poly(aryl ether ketone) with sulfonic groups have received extensive attention for their potential usage as high performance gas dehumidification and ion exchange membrane materials<sup>1,2,3</sup>. Poly (phthalazinone ether ketone)<sup>4</sup>, one of poly(aryl ether ketone), shows excellent comprehensive properties and outstanding thermal stability, whose glass transition temperature is 263°C. It can be soluble in some solvents such as N-methyl-2-pyrrolidone (NMP), N, N-dimethylacetamide (DMAc) and chloroform. In this letter, we report sulfonation of 1, 2-dihydro-4-(4-hydroxyphenyl) (2H) phthalazin-1-one (DHPZ), and the synthesis of sulfonated poly(phthalazinone ether ketone) *via* direct polymerization. The sulfonated 1, 2-dihydro-4-(4-hydroxyphenyl)(2H)phthalazin-1-one (SDHPZ) was prepared as shown in **Scheme 1**.

**Scheme 1** Synthesis of SDHPZ

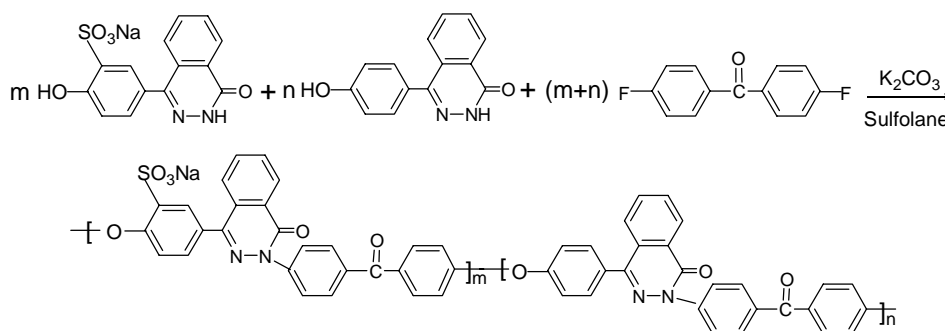


DHPZ was sulfonated in concentrated sulfuric acid at 115°C for 4 hours. The solution was poured into water, and neutralized by sodium chloride. The sulfonated monomer was generated by recrystallization from the mixture of ethanol/water.

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Structure of sulfonated monomer (SDHPZ) was confirmed with FTIR and  $^1\text{H-NMR}$  analysis. The FT-IR spectrum of SDHPZ showed the characteristic peak at  $1652\text{cm}^{-1}$  of  $\text{C}=\text{O}$ , and  $\text{SO}_2$  in sodium sulfonate group at  $1033\text{cm}^{-1}$ , which was absent in the FT-IR spectrum of DHPZ. In the  $^1\text{H-NMR}$  spectrum of SDHPZ and DHPZ, the presence of sulfonic acid group cause a significant down-field shift of signal of hydrogen in hydroxyl group from 9.58 ppm to 10.64 ppm, and the peak area of hydrogen next to HO group in SDHPZ was half of it in DHPZ. Experimental elemental analysis results were also in good agreement with the calculated data: [calcd for  $\text{C}_{14}\text{H}_9\text{N}_2\text{O}_5\text{SNa}\cdot 2\text{H}_2\text{O}$ : C, 44.68%, H, 3.48%, N, 7.44%, Found C, 45.04%, H, 3.23%, N, 7.49%].

**Scheme 2** Synthesis of SPPEK



The poly(phthalazinone ether ketone) containing sodium sulfonate groups (SPPEK) was synthesized *via* direct polymerization from SDHPZ, DHPZ and 4, 4'-difluorodiphenyl ketone (DFDPK) (**Scheme 2**). The polymerization was carried out at  $190^\circ\text{C}$  for 30 h. High molecular weight polymers were obtained in quantitative yield. When the ratio of SDHPZ, DHPZ and DFDPK was 3:7:10 (molar ratio), the polymer with intrinsic viscosity of 1.15 dL/g was obtained in N, N-dimethylacetamide at  $25^\circ\text{C}$ . The intrinsic viscosity of polymer decreased with an increase in the quantity of SDHPZ. The structures of polymers were characterized with FT-IR and  $^1\text{H-NMR}$ . The FT-IR spectrum of SPPEK showed the presence of strong absorption of carbonyl group at  $1666\text{cm}^{-1}$ , aromatic  $\text{C}=\text{C}$  at  $1595\text{cm}^{-1}$ ,  $1504\text{cm}^{-1}$  and  $\text{C}-\text{O}-\text{C}$  at  $1244\text{cm}^{-1}$ , and no absorption of  $\text{O}-\text{H}$ ,  $\text{N}-\text{H}$  at  $3500-3050\text{cm}^{-1}$  could be observed. The  $^1\text{H-NMR}$  spectrum showed the peaks ranging from 7.1 ppm to 8.5 ppm were attributable to aromatic hydrogen. The peak of hydrogen at 7.14 ppm and at 7.35 ppm decreased with increasing of the monomer SDHPZ, while the peak of hydrogen at 8.43 ppm increased. The peaks of  $\text{N}-\text{H}$  and  $\text{O}-\text{H}$  groups at 12.55, 9.58, 10.64 ppm respectively, were absent in  $^1\text{H-NMR}$  spectrum of polymer SPPEK. These results proved that SPPEK was obtained. The temperature of 5% weight loss is above  $480^\circ\text{C}$ . The polymer showed good solubility in some organic solvents such as chloroform, dimethyl sulfoxide, N,N-dimethylacetamide and N-methyl-2-pyrrolidone.

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