

Synthesis and Characterization of Poly (Aryl Ether Ketone) Containing Phthalazinone and Naphthalene Moieties

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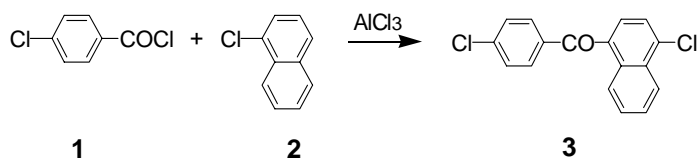
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Abstract: A novel poly (aryl ether ketone) (PPEK) containing phthalazinone and naphthalene moieties was prepared by the nucleophilic displacement reaction of 4-(4-hydroxyphenyl) (2H) phthalazin-1-one with 1-chloro-4-(4-chlorobenzoyl) naphthalene. The polymer was characterized by FTIR, $^1\text{H-NMR}$, DSC, TGA and WAXD.

Keywords: Engineering thermoplastics, poly (aryl ether ketone), synthesis.

Poly (aryl ether ketone)s (PAEKs) are one of the most important high performance engineering thermoplastics, widely used in electronic, electric, aircraft and aerospace industries. ICI' PEEK has enjoyed much commercial success due to its high operating temperature and superior strength. It has a T_g of 143°C , a T_m of 334°C and it is quite solvent resistant. There is a growing demand for new materials to meet increased performance requirements in many areas. Thus there has been considerable research effort made toward the modification of known poly (aryl ether)s¹ as well as the design of polymers with novel structures². Earlier work of ours³⁻⁶ demonstrated that the polymer containing a phthalazinone moiety in the repeat unit was noncrystalline, soluble in some organic solvent and its T_g was 263°C .

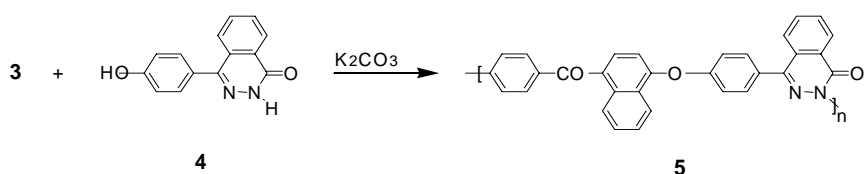
Scheme 1



In this letter, we synthesized an unsymmetric monomer **3**⁷ by introducing 1,4-naphthylene (Scheme 1). The monomer **3** was prepared from *p*-chlorobenzoyl chloride and 1-chloro-naphthalene by the Friedel-Crafts reaction. The high pure monomer was recrystallized from cyclohexane and ethanol. Its structure was confirmed by FTIR, NMR. The poly (aryl ether ketone) was synthesized from monomer **3** and 4-(4-hydroxyphenyl) (2H) phthalazin-1-one (Scheme 2). The polymer was obtained in

quantitative yield with inherent viscosity of 0.38 dL/g in chloroform at 25°C. The structure of the polymer was confirmed by spectroscopic means. The FTIR spectrum showed the C-O-C stretching at 1240.2 cm⁻¹, no C-Cl stretching of monomer **3** at 1093.9cm⁻¹ and almost no O-H, N-H stretching of monomer **4** at 3500-3050 cm⁻¹ appeared. These proved that the nucleophilic

Scheme 2



displacement occurred, and resulted in the formation of C-O and C-N bonds. FTIR also showed the conjugated C=O stretching at 1668.0 cm⁻¹. The ¹H-NMR of the polymer indicated the peaks ranged from 8.65 to 6.85 ppm. The peaks of the protons attached to the nitrogen atom at 12.55 ppm and to the oxygen at 9.58 ppm of the monomer **4** could no longer be found. The Tg was 287°C. The onset temperature taken at 5% weight loss in nitrogen was 484°C. WAXD analysis showed that the polymer was amorphous. The polymer was fully soluble in nitrobenzene, 1,1,2,2-tetrachloroethane, 1-methyl-2-pyrrolidone, CHCl₃ and partially soluble in *o*-dichlorobenzene, *N,N*-dimethylacetamide, *N,N*-dimethylformamide, pyridine and tetrahydrofuran.

Acknowledgments

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References and Notes

1. S. K. Brownstein, M D Guiver, *Macromolecules*, **1992**, 25, 5181.
2. F. W. Mercer, M M Fone, M T Mckenzie, *J. Polym. Sci. Part A*, **1997**, 35, 251.
3. Y. Z. Meng, X G Jian, *Polymeric Materials Science and Engineering*, **1994**, 10, (2), 22.
4. Y. Z. Meng, X G Jian, *Polymeric Materials Science and Engineering*, **1994**, 10, (6), 85.
5. Y. Z. Meng, X G Jian, *Polymeric Materials Science and Engineering*, **1995**, 11, (3), 65.
6. Y. J. Liu, X G Jian, *Acta Polymerica Sinica*, **1999**, (1), 37
7. Selected data of monomer **3**: m.p.:122-123°C, FTIR (KBr,cm⁻¹): 1645.1 (C=O), 1093.9 (C-Cl), 1507.6, 1558.0, 1607.8 (Ar-H); UV (nm): 262.0, 313.0,236.0, 293.0; ¹H NMR (90MHz, CDCl₃) δ : 8.340 (m, 1H), 8.053 (m, 1H), 7.735 (d, 2H, J: 8.79Hz), 7.379 (d, 2H, J: 8.79Hz), 7.65-7.25 (m, 4H), ¹³C NMR (22.5MHz, CDCl₃) δ : 195.7, 140.1, 136.6, 135.6, 135.3, 132.1, 131.8, 131.2, 129.0, 128.2, 127.8, 127.5, 126.2, 125.0, 124.9; DEPT135 δ : 131.8, 129.0, 128.2, 127.8, 127.5, 126.2, 125.0, 124.9.

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