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Synthesis, Characterization and Properties of Poly(aryl amides) Containing Methoxy Substituted Phthalazinone Moiety

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Abstract: A novel aromatic diamine, 1, 2-dihydro-2-(4-aminophenyl)-4-[3-methoxy-4-(4-amino-phenoxy)]-2, 3-phthalazin-1-one (OO-DA) containing aza heterocyclic structure was synthesized from the bisphenol-like monomer in two steps and used for preparing new aromatic polyamides with high inherent viscosity of 0.89-1.03 $dL \cdot g^{-1}$. The structures of diamine and polymers obtained were confirmed by MS, FT-IR, WAXD and ^{1}H-NMR. The synthesized polymers exhibited high glass transition temperature in the range of 281-307 ℃ and good solubility in polar solvents.

Keywords: Poly(ether amide) s, phthalazinone, solubility.

Having high-temperature resistance and excellent mechanical properties, aromatic polyamides have attracted much attention from academic and commercial field, but their applications were partially confined in some fields due to their poor solubility. Now more and more works have been focused on the synthesis of rigid-rod polyamides with good solubility[1-3]. These studies include introducing flexible segments into the polymer chain, introducing bulky pendant groups to minimize crystallization, and forming a noncoplanar structure to make crystallization to be impossible. In this work, we intend our investigation to synthesis poly(ether amide)s containing phthalazinone with bent non-coplanar phthalazinone moiety and flexible methoxy side group, which exhibit good solubility and higher glass transition temperature.

The synthetic procedure of OO-DA was described as follows. A mixture of 4-(3-methoxy-4-hydroxybenzoyl)phthalazin-1-one(2H)(0.091 mol) and *p*-chloronitrobenzene (0.200 mol) in the presence of K_2CO_3 (0.237 mol), DMAc 140 mL, toluene 150 mL was gradually heated to reflux for 8 hrs under N_2 atmosphere. After cooling to room temperature, the yellow dinitro-compound was collected by filtration.(yield: 95.9%, m.p: 198-200℃). The dinitro-compound and hydrazine monohydrate and 5% Pd-C were dissolved in methyl ether glycol and continued to reflux for 8 hrs. After cooling, the precipitated yellow needle crystal OO-DA was separated and recrystallized from methyl ether glycol(yield 85.9%, m.p:213-215). The equal mole diamine and diacid(3 mmol), some dried calcium chloride(1.2 g), triphenyl phosphate(TPP, 2 mL), pyridine(Py, 2 mL) were dissolved with N-methylpyrrolidone(NMP, 8 mL) by the Yamazaki phthosphorylation method[4]. The resulting mixture was reacted at 110℃ and the reaction system was

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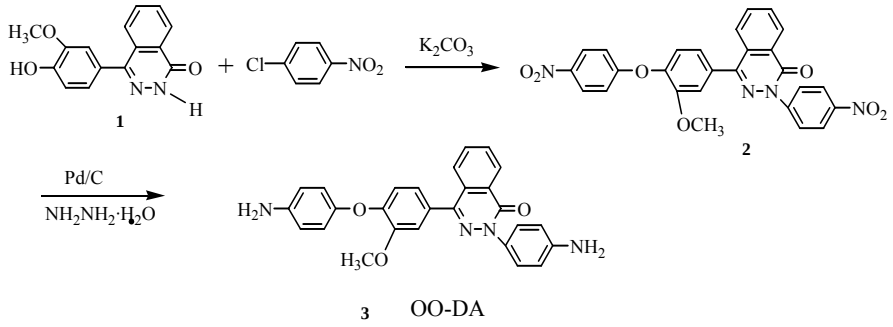
Scheme 1



Scheme 2

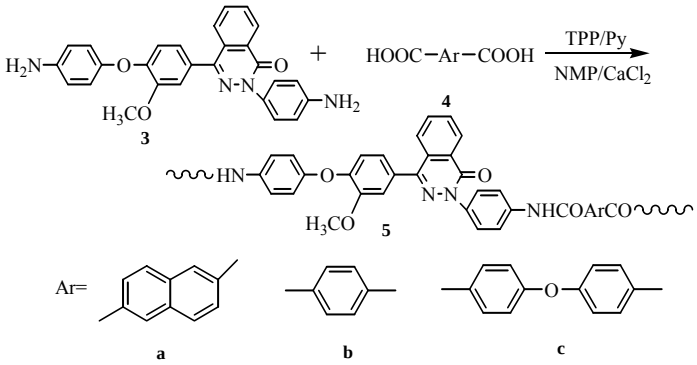


Table 1 Synthesis and characterization data of the polymers

Polym.	η_{inh}[a] dL/g	Yield %	FT-IR ν/cm^{-1}	^{1}H-NMR δ ppm	Tg[b] ℃	T_d[c] ℃
5a	1.03	98	3417(CON-H);1653(C=O) 1226(C-O-C)	7.02-8.70(m,21H,Ar-H) 10.52-10.71(m,2H,N-H)	307	448
5b	1.01	99	3310(CON-H);1666(C=O) 1263(C-O-C)	7.00-8.46(m,19H,Ar-H) 10.39,10.60(s,2H,N-H)	306	443
5c	0.89	98	3427(CON-H);1665(C=O) 1236(C-O-C)	6.98-8.45(m,23H,Ar-H) 10.24,10.43(s,2H,N-H)	281	443

[a] Measured in DMAc with the concentration of 0.5 g·dL^{-1} at 25℃.
[b] Detected by DSC at a heating rate of 20℃/min in nitrogen.
[c] 5% Weight loss temperature in nitrogen.

homogeneously transparent. The viscosity of the solution increased to gelation after 1 h and the inherent viscosity reached the maximum after 3 hrs. So the mixture was poured into 200 mL methanol and the white polymer was obtained. The polymers were purified from dimethylacetamide(DMAc). The result and corresponding data were listed in **Table 1**.

Spectroscopic data conformed the structure of polyamides and all polyamides were soluble in polar solvents such as NMP, DMAc, DMF, DMSO(**Table 1**) *etc.*. All the

polymers showed amorphous nature by WAXD diffraction patterns and high heat-resistant temperature(**Table 1**). Transparent and flexible films were easily cast from DMAc solution.

Acknowledgments

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References and Notes

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5. Notes: compound OO-DA, IR(KBr, cm^{-1}): 3382, 3340(NH_2), 2934(-OCH_3), 1654 (C=O), 1260 (C-O-C); ^{1}H-NMR(400 MHz, DMSO-d_6, δ ppm): 4.95, 5.33(s, 4H, -NH_2), 3.83(s, 3H, -CH_3), 6.58-8.42(m, 15H, Ar-H); MS(*m/z*): 450.5$(M)^+$, Calcd. 450.49.

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