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Synthesis and Characterization of Poly(ether amide)s Containing Bisphthalazinone and Ether Linkages

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Abstract: A novel aromatic diacid, 4, 4'-bis[2-(4-carboxyphenyl)phthalazin-1-one-4-yl]-bisphenyl ether **III**, containing bisphthalazinone and ether linkages was prepared from nucleophilic substitution of *p*-chlorobenzonitrile with the bisphenol-like monomer **I**, followed by alkaline hydrolysis of the intermediate dinitrile **II**. A series of poly(ether amide)s containing bisphthalazinone and ether linkages derived from diacid **III** and aromatic diamines were synthesized by one-step solution condensation polymerization using triphenyl phosphite and pyridine as condensing agents. Moreover, the properties of poly(ether amide)s including thermal stability, solubility and crystallinity were also studied.

Keywords: Poly(ether amide) s, bisphthalazinone, thermal stability, solubility.

Wholly aromatic polyamides are characterized as highly thermally stable polymers with a favorable balance of physical and chemical properties. However, rigidity of the backbone and strong hydrogen bonding result in high melting temperatures or glass-transition temperatures (T_g′s) and limited solubility in most organic solvents[1,2]. These properties make them generally intractable or difficult to process, restricting their applications. Therefore, a great deal of effort has been expended to improve the processing characteristics of the relatively intractable polymers[3-5]. These studies include introducing flexible segments into the polymer chain, introducing bulky pendant groups to minimize crystallization, and forming a noncoplanar structure, thereby making crystallization impossible.

Phthalazinone and its derivatives were reported as non-coplanar bisphenol-like monomers. In our early work[5-8], many polymers containing phthalazinone moieties have excellent properties including high glass transition temperatures, thermal stability, good solubility in many organic solvents and mechanical property. In this letter, we intend our investigation to synthesis poly(ether amide)s containing bisphthalazinone and ether linkages.

A novel aromatic diacid **III** was synthesized by condensation of bisphenol-like monomer **I** with *p*-chlorobenzonitrile in the presence of potassium carbonate, giving corresponding dinitrile compound **II**(**Scheme 1**), followed by alkaline hydrolysis. The structures of dinitrile **II** and diacid **III** were revealed by FTIR, ^{1}H NMR, ^{13}C NMR,

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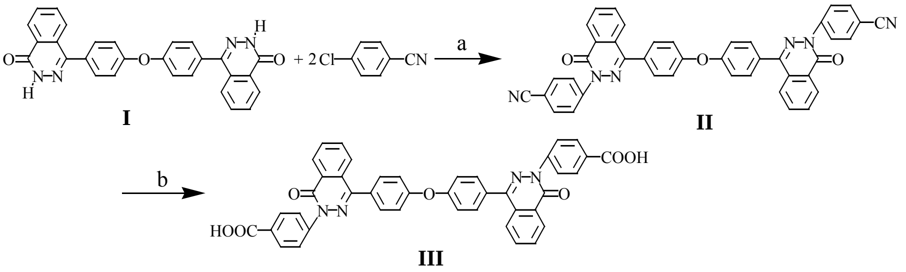
2D-NMR and MS[9,10]. All the obtained data agree with the proposed structures.

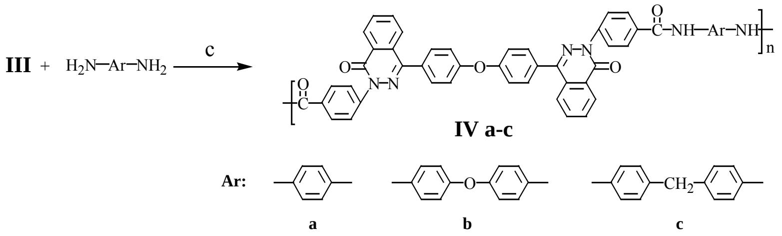
The phosphorylation technique developed by Yamazaki and coworkers[11] was used to prepare polyamides **IV a-c** from diacid **III** with aromatic diamines. Structures and codes of the polymers prepared are shown in **Scheme 2**. Spectroscopic data, together with intrinsic viscosities and T_g measurements, confirming the structures of polyamides are given in **Table 1**.

Scheme 1



Reagents and conditions: a) K_2CO_3, DMAc; b) KOH, H_2O/EtOH.

Scheme 2



Conditions: c) $-H_2O$.

Table 1 Synthesis and characterization data of the polymers (**IVa-c**)

Polymer	FTIR (cm^{-1})	T_g[a] (℃)	T_d[b] (℃)	Yield (%)	η_{inh} ($dL \cdot g^{-1}$)[c]
IV a	3306(N-H), 1668(amide), 1602(C=N)	324	492	98	0.32
IV b	3315(N-H), 1669(amide), 1600(C=N)	319	486	97.6	0.29
IV c	3315(N-H), 1668(amide), 1601(C=N)	319	482	97.2	0.27

[a] Baseline shifts in the second heating DSC traces with a heating rate of 20℃/min in nitrogen.

[b] Decomposition temperatures at which a 10% weight loss was recorded by TG at a heating rate of 20℃/min in nitrogen.

[c] Measured in *N*-methyl-2-pyrrolidone at 25℃ on 0.5 g/dL.

The polyamides had the glass transition temperatures of 319-324℃. These polymers do not loss weight in 10% bellow 480℃. The high glass transition temperatures and thermal stability probably attributed to their rigid bent bisphthalazinone units in polymer backbone. Moreover, almost all the polymers are soluble in aprotic polar solvents, such as NMP and DMAc, due to their heterocyclic moieties and ether linkages in the main chain.

In summary, novel amorphous poly(ether amide)s containing the bisphthalazinone moiety were prepared through the phosphorylation method. The polymers showed outstanding thermal stability, good solubility and film-forming properties.

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9. Compound **II**: mp: 306-307℃. Yield: 88.8%. IR (cm^{-1}): 1250 (m, C-O-C), 1600 (m, C=N), 1675 (s, C=O), 2229 (m, -CN). EI-MS (*m/z*, relative intensity %): 661.5 (M^-, 100%). ^{1}H NMR (400MHz, DMSO-d_6, δ ppm): 7.32 (4H), 7.77 (4H), 7.84 (2H), 8.00 (12H), 8.48 (2H). ^{13}C NMR (400MHz, DMSO-d_6, δ ppm): 158.04, 157.22, 147.07, 145.33, 134.25, 132.72, 132.44, 131.46, 129.84, 128.48, 128.02, 127.16, 126.42, 118.91, 118.45, 109.81.
10. Compound **III**: mp: 348-349℃. Yield: 87%. IR (cm^{-1}): 1243 (m, C-O-C), 1591 (m, C=N), 1679 (s, C=O), 3070 (m, -COOH). EI-MS (*m/z*, relative intensity %): 697.5 (M^+, 100%). ^{1}H NMR (400MHz, DMSO-d_6, δ ppm): 7.30 (4H), 7.74 (4H), 7.81 (2H), 7.89 (4H), 7.95(4H), 8.08 (4H), 8.45 (2H), 13.07 (2H). ^{13}C NMR (400MHz, DMSO-d_6, δ ppm): 166.46, 157.73, 156.98, 146.50, 144.97, 133.78, 132.03, 131.24, 129.76, 129.45, 129.28, 128.22, 127.93, 126.95, 126.66, 125.33, 118.72.
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