Synthesis and Characterization of Novel Aromatic Polyamides via Yamazaki-Higashi Phosphorylation Method

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Abstract

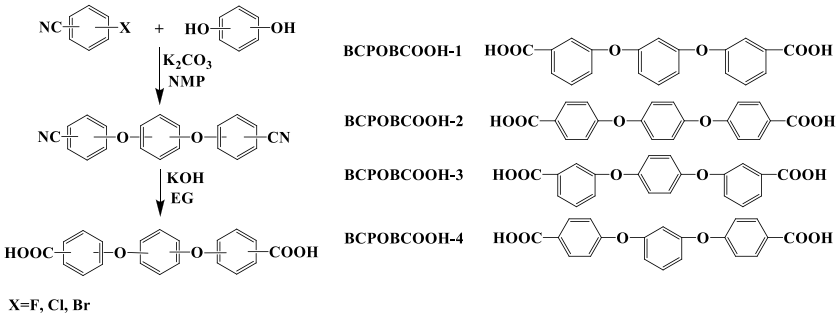

Fig 1 fig the chemical route for the production of diacids

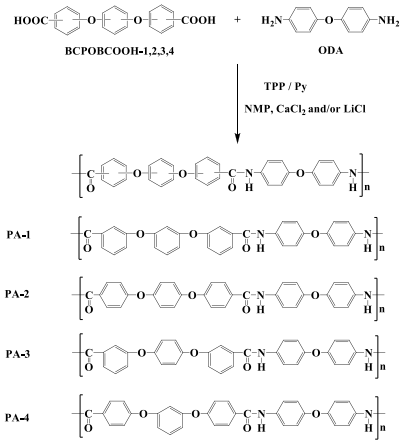

Fig 2 the procedure for the synthesis of PA

Based on a previously reported procedure, we synthesized four aromatic diacids: 1,3-bis(3-carboxyphenoxy)benzene, 1,4-bis(4-carboxyphenoxy)benzene, 1,4-bis(3-carboxyphenoxy) benzene, and 1,3-bis(4-carboxyphenoxy)benzene with high purity (Fig 1). As shown in Fig2, with the presence of triphenylphosphite (TPP), pyridine (Py) and halide salts, several new kinds of aromatic polyamides were prepared by the direct polycondensation reactions of the aromatic diamine 4,4'-oxydianiline (ODA) with four synthesized aromatic dicarboxylic acid in quantitative yields. The PAs have inherent viscosities between 0.5 and 1.0 dL/g, which shows that the obtained polymers have high molecular weight. The obtained polyamides were then characterized by FT-IR and ^{1}H NMR analyses. FTIR shows the characteristic absorption bands in the range of 3500~3000 cm^{-1} assigned to the N-H stretching of amide band and the C-H stretching of benzene rings. The absorption band around 1525 cm^{-1} is assigned to C-N stretching and N-H bending vibration of amide Ⅱ band. The absorption band around 1254 cm^{-1} is assigned to C-C=O stretching and N-H bending vibration of amide Ⅲ band.

The absorption band around 706 cm^{-1} is assigned to N-H out-of-plane formation vibration of amide Ⅳ band. The absorption band at 1230 cm^{-1} is assigned to aryl–ether–aryl (C-O-C) symmetrical stretching in the polymer backbone. The peak assignments obtained from ^{1}H NMR spectra are in good agreement with the proposed chemical structures. For solubility, all four PAs are soluble in polar solvents, such as dimethylsulfoxide (DMSO), N,N-dimethylacetamide (DMAc), N-dimethylformamide (DMF), 1-methylpyrrolidone (NMP), and so on. This good solubility would facilitate the fabrication of PA film based solution casting method. Good thermal stability properties were also determined by thermogravimetric analysis (TGA) under a nitrogen atmosphere at a heating rate of 20 °C·min^{-1}. The decomposition temperature of obtained polymers was higher than 400 °C. The amount of carbonized residue of these polymers in nitrogen atmosphere was more than 55% at 800 °C, which might be ascribed to their high aromatic content. All the casting films exhibit tensile strengths, Young's modulus and elongations at break, in the ranges of 87-147 MPa, 2.6-5.5 GPa and 4.4-8.7%, respectively. Based on the results of mechanical properties, it is observed that polyamide-1 showed the best mechanical properties, with the max stress up to 147 MPa and a modulus of 5.5 GPa. It is also interesting to found that the films of PA-1, PA-2 and PA-3 are completely transparent in the visible range, while PA-4 film is opaque which is attributed to the Crystallization of PA-4 film. The crystallinity of these polyamides was investigated by the microscope with parallel and crossed polarizers(POM). In the heating process, PA-4 began to melt at 380 ^{o}C, while other three polyamides melt at lower temperature below 300 ^{o}C. For PA-1, PA-2 and PA-3, they just showed a bright-field at some extent, while obvious crystallinity could easily be seen in (d) PA-4. The POM result indicated that PA-1, PA-2, PA-3 were hard to crystalline, while PA-4 was highly crystalline.

Keywords: phosphorylation reaction; aromatic polyamide

Table 1 the mechanical properties of polyamides

Polymers	Max Stress[a] (MPa)	Elongation at Break[a] (%)	Young's modulus （GPa）
PA-1	147	4.4	5.5
PA-2	87	8.1	2.6
PA-3	129	8.0	3.4
PA-4	132	8.7	4.3