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Novel Polyamides Containing Biphenyl-phthalazinone Moieties

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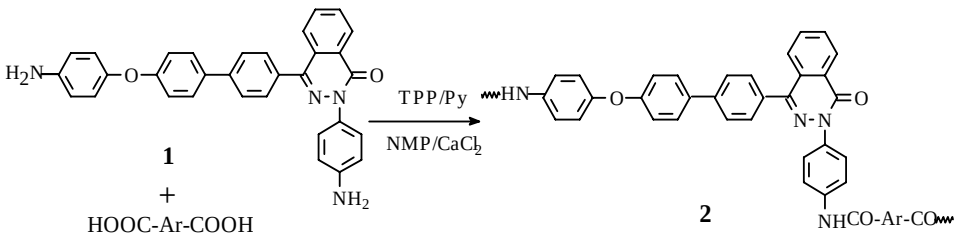
Abstract: A novel diamine monomer 2H-(4-aminophenyl)-4-[4-(4-aminophenoxy) biphenyl]-phthalazinone **1** containing aza hetero cycle was synthesized and utilized for preparation of new high molecular weight aromatic polyamides with various aromatic dicarboxylic acids with the inherent viscosity of 0.50 ~ 1.62 g/dL. These polyamides had rather high glass transition temperatures of 327~356℃ and their structure was confirmed by IR, ^{1}H NMR and MS. They are readily soluble in polar solvents such as NMP, DMF *etc*. and easily cast into tough, flexible films.

Keywords: Polyarylamide, biphenyl-phthalazinone, solubility, thermostability.

Aromatic polyamides are characterized by the good mechanical strength and excellent thermal and oxidative stability but have limited solubility. Maintaining their thermal stability, considerable effort has been made towards the improvement of their solubility and processability through structural modification at the molecular level such as the introduction of bulky naphthalene moiety, an unsymmetric unit, a pendant group or a heterocycle moiety into the polymer backbone[1~3]. In this work, we report the synthesis of novel polyarylamide with rigid rodlike biphenyl and bent phthalazinone moieties and with higher glass transition temperature (T_g = 356°C).

Scheme 1 The synthetic route of poly(aryl amide)s



The novel poly (ether amide)s containing biphenyl phthalazinone were prepared by direct polymerization of **1** with different aromatic dicarboxylic acids. In IR spectrum, the sharp double peak at 3306, 3462 cm^{-1} derived from primary amine(-NH_2) of

compound **1** became weak single peak of secondary amine of polyamides (-NH-) **2a**, **2b** and **2c**. In ^{1}H NMR spectrum, the strong peak at δ 4.86 ppm assigned to primary amine (-NH_2) of diamine monomer **1** shifted to δ 10.34~10.50 ppm for –NHCO- in polyamides. The data of IR, ^{1}H NMR and MS correspond with the structure of diamine monomer of **1** and the polyamides of **2a**, **2b** and **2c**[4].

The properties of **2** were examined and listed in **Table 1**:

Table 1 The properties of poly (biphenylphthalazinone ether amide)s

Polymer	Yield %	η^{a}_{inh} dl.g^{-1}	Tg^{b} ℃	TGA^{C} ℃
2a	98.0	0.52	356	415
2b	96.0	0.50	327	449
2c	99.5	1.62	330	-

a: The inherent viscosity of **2** was detected in DMAc with a concentration of 0.5 g dl^{-1}at 30℃.
b: Detected by DSC at a heating rate of 10℃ / min in nitrogen.
c: 10 % weight loss temperature in nitrogen.

The polyamide **2a** had the glass transition temperature of 356°C, which was increased 29°C than that of polymer's reported in previous work[3], and the T_g of **2c** was 330°C. These polymers do not loss weight in 10% bellow 415°C. The high glass transition temperature and thermostability probably attributed to their rigid bent phthalazinone and rodelike biphenyl units in polymer backbone. Also they can dissolve in aprotic polar solvents such as NMP, DMAc due to their unsymmetric angular polymer chain. Clear tough films were cast from DMAc solution of polyamides. Therefore, these polymers are expected to apply in the fields of heat resistance separation membrane and thermal stable coating *etc*..

References and Notes

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3. X. G. Jian , L. Cheng, *J. Polym. Sci., Part A: Polym. Chem.* , **1999**, *37*(4) ,459.
4. Notes: **1** IR (KBr, cm^{-1}): 3336, 3402 (NH_2), 1656 (C=O), 1246 (C-O); ^{1}H NMR (400MHz, DMSO-d_6, δ ppm): 4.86(s, 4H, NH_2), 6.56 ~ 8.46 (m, 20H, Ar-H); MS (*m/z*): 497.2 (M), 498.1 (M+1), 499.2 (M+2). **2a** IR (KBr, cm^{-1}): 3305 ~ 3264 (NH, amide), 1665, 1630 (amide C=O), 1260 (C-O-C); ^{1}H NMR (400MHz, DMSO-d_6, δ ppm): 10.34, 10.48 (s, 2H, two kind of unsymmetric –CONH-), 7.12~8.46 (m, 24H, Ph-H). **2b** IR (KBr, cm^{-1}): 3265~3293 (amide –NHCO-), 1630 ~ 1666 (amide C=O), 1236 (C-O-C); ^{1}H NMR (400MHz, DMSO- d_6, δ ppm): 10.36, 10.50 (s, 2H, two kind of unsymmetric –CONH-), 7.10 ~ 8.57 (m, 24H, Ph-H). **2c** IR (KBr, cm^{-1}): 3418 (-NH-, amide), 1664, 1602 (-CO-, amide), 1228, 1133 (C-O-C); ^{1}H NMR (400MHz, DMSO- d_6, δ ppm): 10.45, 10.31(s, 2H, two kind of unsymmetric -CONH-), 7.07 ~ 8.63 (m, 24H, Ar-H).

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