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Synthesis of Methyl-substituted Phthalazinone-based Aromatic Poly(amide imide)s

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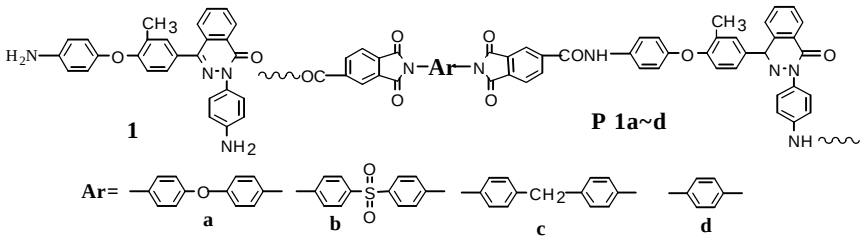
Abstract: A series of novel aromatic poly (amide imide)s containing phthalazinone moieties were prepared from 2-(4-aminophenyl)-4-[3-methyl-4-(4-aminophenoxy)-2,3-phthalazinone-1], a novel diamine **1** with four diimide-dicarboxylic acids by Yamazaki phosphorylation method with the inherent viscosity of 0.36~0.65 dL/g. These polymers had high glass transition temperatures above 300°C and they lost 10% weight between 426~475°C in N_2. The structure of diamine **1** and the polymers was confirmed by IR, ^{1}H NMR and MS. The obtained polymers were readily soluble in polar solvents such as NMP, *m*-cresol *etc.* and easily cast into tough, flexible films. The X-ray indicated that they are all amorphous.

Keywords: Aromatic poly(amide imide), phthalazinone, synthesis, heat-resistance.

Aromatic polyimides are well-known high performance polymers because of their attractive combination of chemical, physical and mechanical properties. But they have limited applications due to their insolubility and infusability. Poly(amide imide)s have deserved particular attention as their good processability and solubility[1~2]. We had reported the synthesis of a novel soluble poly(phthalazinone amide)s[3]. The present work describes the synthesis of novel methyl-substituted poly(ether amide imide)s bearing the twist non-coplanar phthalazinone units in the parent chain.

Scheme 1



2- (4-aminophenyl) - 4- [3- methyl- 4- (4-aminophenoxy)-2, 3-phthalazinone-1] **1,** a novel diamine was synthesized *via* convenient procedure according to the previous method[4]. Thus a series of novel poly (ether amide imide)s containing phthalazinone

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moieties were prepared by direct polycondensation from diamine **1** with four diimide-dicarboxylic acids by Yamazaki phosphorylation method[5] as shown in **Scheme 1**. The polymerization results and the thermal properties of polymers are summarized in **Table 1**. The glass transition temperatures of polymers **P1a** , **P1d** were above 300°C and these polymers did not loss weight in 10% bellow 426°C. The good thermostability probably attributed to their rigid bent phthalazinone units in polymer backbone.

Table 1 The polymerization and thermal properties of poly (ether amide imide)s **P1a~d**

Polymer	Yield %	η_{inh}[a] dLg^{-1}	Tg[b] °C	TGA[c] °C
P1a	98.0	0.47	302	458
P1b	98.0	0.65	-[d]	426
P1c	99.8	0.36	-	475
P1d	99.8	0.41	325	462

a: Detected in DMAc with a concentration of 0.5 dLg^{-1}at 30°C. b: Detected by DSC at a heating rate of 10°C min^{-1} in N_2. c: 10 % weight loss temperature in N_2. d: Not detected.

The structure of diamine monomer **1** and the poly(amide imide)s **P1** was confirmed by IR, ^{1}H NMR and MS. In MS, the molecular peak of diamine **1** $C_{27}H_{22}O_2N_4$ appearing at 435.1 was consistent with the proposed molecular weight. In IR spectrum, the sharp double peak at 3336, 3402 cm^{-1} derived from primary amine(-NH_2) of compound **1** became weak single peak of secondary amine of polymers (-NH-) **P1**. In ^{1}H NMR spectrum, the strong peak at δ 4.86 assigned to primary amine (-NH_2) of diamine monomer **1** shifted to δ 10.50~10.65 for –NHCO- in polymers.

Table 2 The solubility of poly(ether amide imide)s **P1a~d**

Polymer	DMF	DMAc	NMP	DMSO	*m*-Cres	$CHCl_3$	Py	NB	THF	DCB
P1a	+	+	++	+	+	-	++	±	-	-
P1b	+	+	++	+	+	-	++	±	-	-
P1c	+	+	++	+	+	-	++	±	-	-
P1d	-	±	++	-	+	-	-	±	-	-

++: Soluble at room temperature; +: soluble at elevated temperature; ±: partly soluble; -: insoluble.

Table 2 summarized the result of solubility of polymers which indicated that all polymers can dissolve in polar solvents such as NMP, *m*-cresol *etc* due to their unsymmetric angular polymer chain and the methyl-substituents along the main chain. **P1d** had the rather poor solubility because of their rigid rod-like parent chain. Yellow tough films were cast from NMP solution of polymers. The X-ray indicated that they are all amorphous.

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