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Communications to the Editor

Synthesis of All Aromatic Phthalazinone Containing Polymers by a Novel N−C Coupling Reaction

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Introduction. Heterocyclic polymers, such as poly(benzoxazole)s, are high-temperature polymers that show excellent thermal and hydrolytic stability and have received considerable attention as high-modulus fibers. These heterocyclic polymers are constructed with aromatic moieties linked usually by groups which give some flexibility to the polymer chain. Conventionally, two ways have been utilized to synthesize heterocyclic polymers. The first uses the heterocyclic ring formation for the polymerization reaction. Polymers, such as poly(imide)s[1] and poly(oxadiazole)s,[2] are synthesized in this manner. In the second approach catenation of the heterocyclic rings is carried out by condensation reactions. The poly(aryl ether) synthesis by nucleophilic aromatic substitution is one example. In this case the polymer is formed by the reaction of the preformed heterocyclic halides or activated aryl halides with a nucleophile, such as a bis(phenolate) anion, in a nucleophilic displacement reaction. Many different types of high-temperature heterocyclic polymers, such as poly(ether imide)s,[3] poly(aryl ether phenylquinoxaline)s,[4] and poly(aryl ether benzoxazole)s,[5] have been synthesized by this method.

Polymers with the N−N bond in the polymer chain,[6] as well as polymers whose heterocycle contains the N−N linkage, have been previously synthesized.[7] Imai reported the synthesis of poly(pyridazinophthalazinedione)s, which have high thermostability, from dibenzoylphthalic acids and bis(aryl)hydrazines.[8]

Methods to form the carbon−nitrogen bond in aromatic systems are limited to rather vigorous processes which are copper mediated.[9,10] To the best of our knowledge, no polymerization reaction using the aza nitrogen anionic displacement has been reported outside our laboratory.

In previous papers we have described the synthesis of poly((1,2-dihydro-1-oxo(2*H*)-phthalazine-2,4-diyl)-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenylene) (**1**) by the reaction of 1,2-dihydro-4-(4-hydroxyphenyl)-1(2*H*)-phthalazinone (**2**) with bis(4-fluorophenyl) sulfone (Scheme 1).[11] This reaction suggested to us that compounds with two phthalazinone groups would be potential monomers for polymerization in a nucleophilic substitution reaction because the phthalazinone NH groups behave like phenolic OH groups. In this paper we describe the synthesis of phthalazinone monomers and their reactivity. The thermal properties of the formed poly(phthalazinone)s are also described briefly.

Results and Discussion. Biphthalazinone monomers **5b**−**e** and 2,3,7,8-tetraazaanthracenediones **5a** were synthesized from the corresponding dianhydrides in two steps according to Scheme 2. 4,4′-Oxydiphthalic anhydride **3c** was subjected to Friedel−Crafts reaction with benzene to produce the dicarboxylic acids **4** in 60% yield. The mixture of isomers was then treated with a slight excess of hydrazine monohydrate in DMF to yield the 1,1′-dioxo-4,4′-diphenyldiphthalazinone ether **5c** in 90% yield. The solid product was recrystallized from glacial acetic acid to give a white powder. The other monomers were synthesized in the same way. All the monomers except **5a** showed sharp single melting points in the DSC between 350 and 400 °C. Mixtures of three isomers of **5b**−**e** would be expected; however, the monomers are very insoluble and therefore difficult to analyze. Only in the case of **5a** were we able to separate the expected two isomers (mp 278 and 310 °C) by fractional recrystallization from glacial acetic acid.

Scheme 1

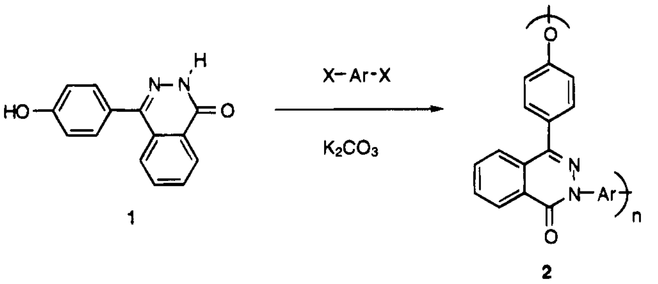

Table 1. Phthalazinone Polymers

polymer	chemical shift of NH (ppm)	solvent	temp (°C)	yield (%)	η_{inh}[a] (dL/g)	solvent
9a	12.90	DPS	310	99	0.28	H_2SO_4
9b	12.93	NMP/DPS	190	97	0.31	NMP
9c	12.71	NMP/DPS	190	89	0.44	NMP
9d	12.99	DPS	310	92	0.11	NMP
9e	13.13	NMP/DPS	190	0[b]		
10c	12.71	sulfolane/DPS	310	96	0.43	NMP
11c	12.71	DPS	310	98	0.31	NMP

[a] Inherent viscosities were measured at a concentration of 0.5 g/dL in H_2SO_4 at 25 °C. [b] Insoluble residue formed.

The high molecular weight poly(phthalazinone)s, which are copolymers of the corresponding three phthalazinone isomeric monomers, were prepared by the reaction of the biphthalazinone monomer with bis(4-fluorophenyl) sulfone (**6**) or 4,4′-difluorobenzophenone (**7**) or 2,6-dichlorobenzonitrile (**8**) in a dipolar aprotic solvent. Diphenyl sulfone (DPS) and mixtures (1:1) of DPS with NMP and sulfolane in the presence of potassium carbonate (Scheme 3) proved to be the best solvents for the polymerization reaction. The phthalazinone aza nitrogen anion, which was formed in the deprotonation by potassium carbonate, attacked the activated aryl halides with elimination of fluoride. High molecular weight polymers with inherent viscosities of 0.3−0.4 (see Table 1) were obtained in the reaction between monomers **5b**, **5c**, and **6**. The structure of **5a** is so rigid that even in the reaction with **6**, which forms the most soluble polymer, the insoluble oligomer precipitated out in an early stage of the polymerization reaction. When **7** or **8** is reacted with biphthalazinone

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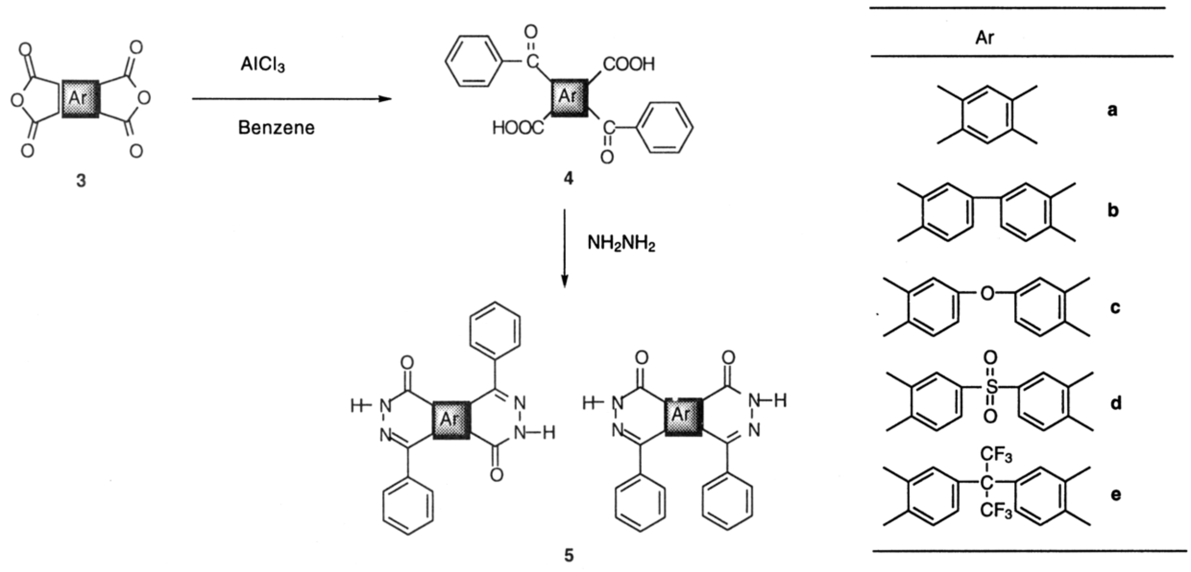
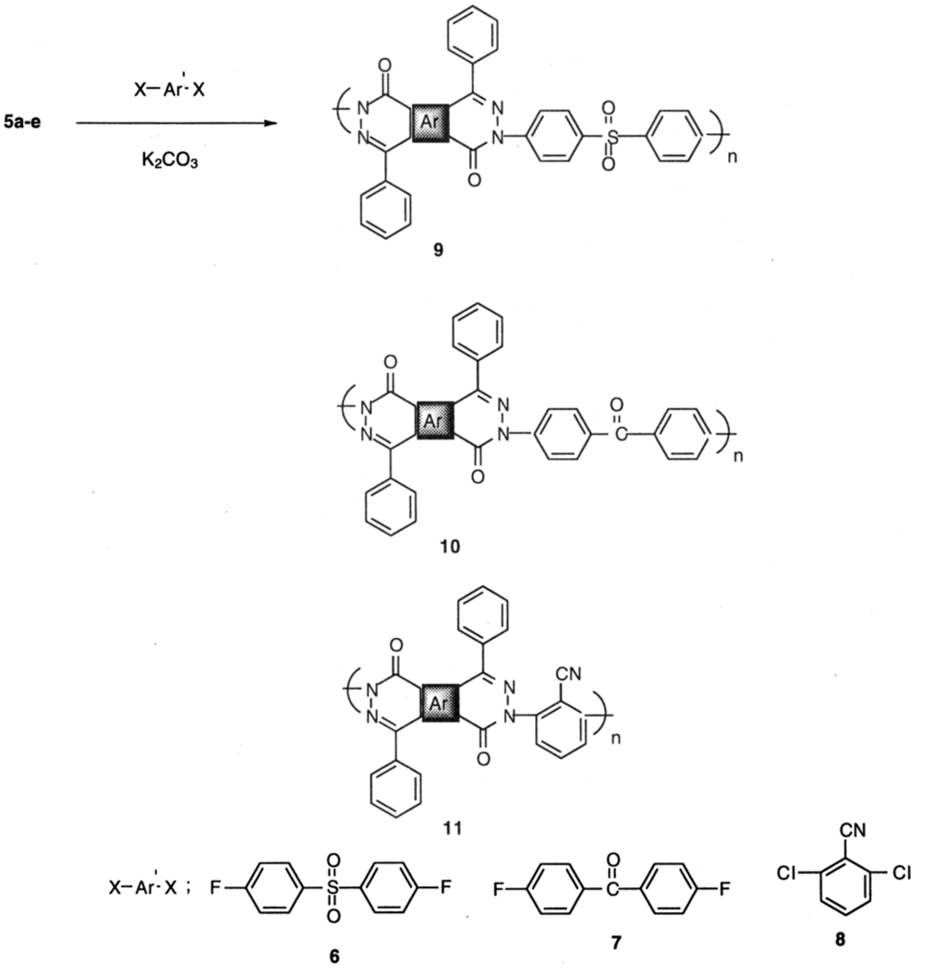
Scheme 2



Scheme 3



monomers, insoluble oligomer precipitated out before high molecular weight polymer formed, except for monomer **5c**. The monomers which have an electron-withdrawing group, such as **5d**,**e**, do not form high molecular weight polymers. The electron-withdrawing group makes the NH group more acidic, and consequently, the resulting anion becomes less nucleophilic; therefore, the polymerization does not proceed. Most of the polymers synthesized are soluble in NMP. Polymers **9c** and **10c** were cast into flexible films from

Table 2. Thermal Properties of Phthalazinone Polymers

polymer	T_g (°C)	TGA (°C)[a] air	TGA (°C)[a] N$_2$
9a		478	488
9b	344	478	479
9c	310	485	499
10c	286	512	497
11c	301	531	526

[a] Reported for 5% weight loss.

m-cresol. Polymer **9a** is soluble only in a solvent such as concentrated sulfuric acid. All the polymers obtained show characteristic phthalazinone CO stretching at 1650 cm^{-1} in their IR spectra.

The glass transition temperatures (T_g's) listed in Table 2 were measured by differential scanning calorimetry (DSC). The poly(phthalazinone)s showed very high T_g's around 300 °C. The T_g of polymer **9a** was not detectable by DSC. Thermal stabilities of the poly(phthalazinone)s showed a similar pattern of decomposition with no weight loss below 400 °C in either air or nitrogen. The temperatures for 5% weight loss were observed between 480–530 °C.

In conclusion, a new class of monomers, bisphthalazinones, have been prepared in two steps in high yield from readily available compounds. They were reacted with a series of activated aryl halides to give high molecular weight novel poly(phthalazinones) in a one-step reaction involving the formation of a N–C bond. The formed polymers show high glass transition temperatures and excellent thermostabilities. Some of them are soluble in organic solvents such as NMP.

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