

Synthesis and Reactions of *N*-Phenylated Polyamine Derived from α,α' -Dibromo-*p*-xylene and Aniline

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ABSTRACT: *N*-Phenylated polyamine was synthesized by the solution polycondensation of α,α' -dibromo-*p*-xylene with aniline, α,α' -dianilino-*p*-xylene, and their trimethylsilyl derivatives in *N*-methyl-2-pyrrolidone at 150°C in the presence of potassium bicarbonate as an acid acceptor. Among the amines employed, α,α' -dianilino-*p*-xylene gave the polyamine having the highest inherent viscosity of 0.3 dl g⁻¹. The effects of reaction medium, acid acceptor, reaction temperature, and reaction time were studied. The *N*-phenylated polyamine was amorphous and soluble in chloroform and *sym*-tetrachloroethane. The polymer had a glass transition temperature of 110°C, and was stable up to 280°C in air. The polyamine gave a violet-colored polymer when treated with 4,4'-bis(dimethylamino)benzophenone in the presence of phosphoryl chloride in refluxing dioxane. Also, the polymer formed an insoluble product when reacted with carbon tetrabromide in dioxane solution under ultraviolet light irradiation.

KEY WORDS *N*-Phenylated Polyamine / Synthesis / Solubility / Thermal Behavior / Polymer Reactions / Polymeric Pigment / Negative Resist /

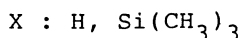
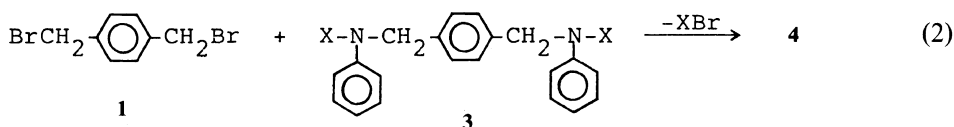
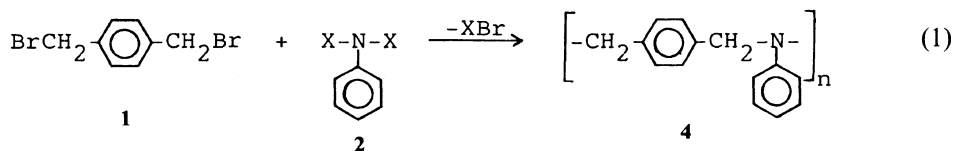
Although most polyamines are generally prepared by the cationic ring-opening polymerization of aziridines,¹ azetidines,¹ and 2-oxazolines,² there are relatively few reports on the synthesis of condensation-type polyamines. Dyer and Anderson reported the indirect synthesis of linear polyamines by the polycondensation of aromatic and aliphatic diamines with terephthalaldehyde giving polyazomethines followed by catalytic hydrogenation.³ For the direct preparation of linear polyamines, it would be highly desirable to use either a primary amine or a di(secondary amine) as a starting material, since di(primary amines) such as hexamethylenediamine and bis(4-aminophenyl) ether might give crosslinked products. Accordingly, the polycondensation of bis(4-fluorophenyl) sulfone with bis(4-piperidyl)-1,3-propane gave linear polyamine

of high molecular weight.⁴ Klebe obtained high molecular weight polyamine by the polycondensation of α,α' -dichloro-*p*-xylene with *N,N'*-bis(trimethylsilyl)-piperazine.⁵ We reported the synthesis of polyarylamines of high molecular weight by the polycondensation of bis(4-chloro-3-nitrophenyl) sulfone with both aromatic and aliphatic diamines.⁶ Further work at our laboratory showed that polyamine derivatives were obtained in low molecular weights by the polycondensation of activated dichloro compounds with benzene-sulfonamide under phase transfer conditions.^{7,8} Quite recently, we synthesized *N*-phenylated polyamides and polyureas of high molecular weights from α,α' -dianilino-*p*-xylene and both aromatic diacid chlorides⁹ and aromatic diisocyanates,¹⁰ respectively. As continuation of these studies, we conducted the synthesis of

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polyamines containing pendant *N*-phenyl groups, and studied their properties. This paper deals with the synthesis and reactions of *N*-

phenylated polyamine from α,α' -dibromo-*p*-xylene and aniline and its derivatives (eq 1 and eq 2).



EXPERIMENTAL

Materials

Commercial α,α' -dibromo-*p*-xylene (**1**) was used as received. Aniline (**2a**) was dried over calcium hydride and distilled under reduced pressure.

N,N-bis(trimethylsilyl)aniline (**2b**) was prepared by the reaction of *N*-(trimethylsilyl)aniline, which was obtained from aniline and trimethylsilyl chloride, with butyl lithium in tetrahydrofuran, followed by treatment with trimethylsilyl chloride¹¹; bp 38–40°C/0.1 Torr (lit.¹¹ bp 98–99°C/11 Torr).

α,α' -Dianilino-*p*-xylene (**3a**) was synthesized by the reaction of *p*-xylene- α,α' -diol with aniline in the presence of potassium hydroxide¹⁰; mp 125–127°C (lit.¹⁰ mp 125–126°C).

N,N'-Bis(trimethylsilyl)- α,α' -dianilino-*p*-xylene (**3b**) was prepared from **3a** and trimethylsilyl chloride⁹; mp 88–89°C (lit.⁹ mp 88–89°C).

Inorganic salts such as potassium bicarbonate were used as received. All solvents including *N*-methyl-2-pyrrolidone (NMP) were distilled before use following the usual procedures.

Polymerization

Synthesis of Polyamine 4. A mixture of 1.319 g (5.0 mmol) of **1**, 1.442 g (5.0 mmol) of **3a**, 1.0 g of potassium bicarbonate, and 10 ml of NMP was heated with stirring at 150°C for 24 h under nitrogen. The homogeneous mixture, except for the solid potassium bicarbonate, turned into a white heterogeneous slurry within 15 min from the start of the reaction. The reaction mixture was then poured into 500 ml of water and the precipitated polymer was collected. It was washed several times with water and finally with hot methanol, and dried at 60°C under vacuum. The yield was 1.77 g (90%), and the inherent viscosity of the polymer in *sym*-tetrachloroethane was 0.30 dl g⁻¹, measured at a concentration of 0.5 g dl⁻¹ at 30°C. *Anal.* Calcd for (C₁₄H₁₃N)_n: C, 86.12%; N, 6.71%; N, 7.17%. Found: C, 85.58%; N, 6.19%; N, 7.14%.

Polymer Reaction

To a solution of 0.363 g (0.93 mmol) of polyamine **4** and 0.50 g (1.86 mmol) of 4,4'-bis(dimethylamino)benzophenone in 20 ml of dioxane was added 0.53 g (3.45 mmol) of phosphoryl chloride at once. The contents were heated with stirring at 100°C for 30 min. A

violet color developed as the reaction proceeded. After the reaction, the mixture was poured into 500 ml of water. The colored precipitate was filtered, washed several times with water, and dried at 60°C under vacuum. The yield was 0.353 g (74%).

Polymer Reaction under Ultraviolet (UV) Light Irradiation

A mixture of 0.10 g (0.26 mmol) of polyamine **4** and 0.028 g (0.085 mmol) of carbon tetrabromide was dissolved in 5 ml of dioxane. The solution placed in an UV cell was irradiated using a 400 W high pressure mercury lamp at a distance of 10 cm. The resulting precipitate was filtered, washed several times with dioxane, and dried. The progress of the reaction was followed as a function of time by measuring the amount of the precipitate formed.

Measurements

Infrared (IR) spectra and UV spectra were recorded on a JASCO FTIR-5000 Fourier transform spectrophotometer and a Hitachi U-3400 spectrophotometer, respectively. ¹H-nuclear magnetic resonance (NMR) spectra were obtained on a JEOL JNM-PMX60 NMR spectrometer (60 Hz). Differential thermal analysis (DTA), thermogravimetry (TG), and thermomechanical analysis (TMA, penetration method) were performed with Shimadzu thermal analyzers DTA-40M, TGA-40M,

and TMA-40M, respectively. A wide angle X-ray diffraction pattern was obtained for polymer pellet at room temperature on a Rigakudenki XG X-ray apparatus with nickel-filtered CuK_α radiation (30 kV, 50 mA). Weight-average molecular weight (\bar{M}_w) and number-average molecular weight (\bar{M}_n) were determined by means of gel-permeation chromatography (GPC) on the basis of a polystyrene calibration on a JASCO HPLC BIP-I apparatus (column, Shodex GPC AD-80M/S polystyrene gel; eluent, dimethylformamide containing 0.01 M of lithium bromide; detector, Shodex RI detector).

RESULTS AND DISCUSSION

Polymer Synthesis

In a preliminary study, α,α' -dibromo-*p*-xylene (**1**) was polycondensed with aniline (**2a**), α,α' -dianilino-*p*-xylene (**3a**), and their trimethylsilyl derivatives **2b** and **3b**, respectively, giving *N*-phenylated polyamine according to eq 1 and 2. Among the four amine monomers employed, **3a** gave the polyamine with the highest inherent viscosity of 0.30 dl g⁻¹, when the polycondensation was carried out in NMP at 150°C using potassium bicarbonate as an acid acceptor (Table I). The polymerization with aniline in hexamethylphosphoramide (HMPA) at 20°C also gave the polymer with inherent viscosity of 0.24 dl g⁻¹. Our previous studies showed that the *N*-trimethylsilyl-

Table I. Polycondensation of **1** with aniline and its derivatives (**2** and **3**) giving polyamine ⁴

Amine	Reaction conditions ^a			Polymer	
	Solvent	Acid acceptor	Temperature/°C	Yield/%	η_{inh}^b /dl g ⁻¹
2a	HMPA	NaHCO ₃	20	99	0.24
2b	NMP	—	100	80	0.10
3a	NMP	KHCO ₃	150	90	0.30
3b	NMP ^c	—	100	98	0.26

^a Polymerization was carried out with 5 mmol of each monomer in 10 ml of the solvent in the presence of 1.0 g of the acid acceptor for 24 h.

^b Measured at a concentration of 0.5 g dl⁻¹ in *sym*-tetrachloroethane at 30°C.

^c 1.0 g of KF was added to the reaction mixture.

Table II. Polycondensation of **1** with **3a** in various solvents to give polyamine **4**^a

Reaction medium	Polymer		Remarks ^c
	Yield/%	η_{inh}^b /dl g ⁻¹	
DMAc	90	0.26	Hetero
NMP	99	0.23	Homo
DMSO	89	0.20	Hetero
HMPA ^d	99	0.13	Homo→Hetero
Nitrobenzene	84	0.17	Homo→Hetero
Anisole	85	0.09	Homo

^a Polymerization was carried out with 5 mmol of each monomer in the solvent in the presence of 1.0 g of NaHCO₃ at 100°C for 5 h.

^b Measured at a concentration of 0.5 g dl⁻¹ in *sym*-tetrachloroethane at 30°C.

^c Appearance of the polymerization mixture: Homo, homogeneous solution; Hetero, heterogeneous mixture.

^d Polymerization was carried out at 200°C.

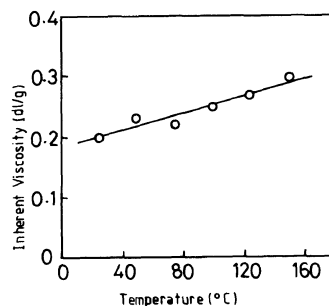
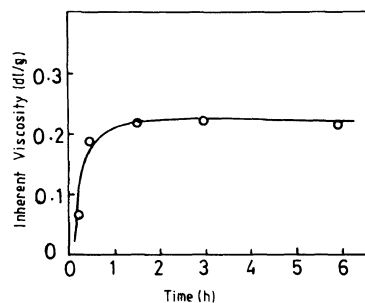
Table III. Polycondensation of **1** with **3a** in the presence of various acid acceptors giving polyamine **4**^a

Acid acceptor	Polymer	
	Yield/%	η_{inh}^b /dl g ⁻¹
NaHCO ₃	90	0.26
KHCO ₃	90	0.30
Na ₂ CO ₃	87	0.17
K ₂ CO ₃	89	0.13

^a Polymerization was carried out with 5 mmol of each monomer in 10 ml of NMP in the presence of 1.0 g of the acid acceptor at 150°C for 24 h.

^b Measured at a concentration of 0.5 g dl⁻¹ in *sym*-tetrachloroethane at 30°C.

substituted diamines were more reactive than the parent diamines toward diacid chlorides, thereby giving higher molecular weight polyamides.^{9,12} Also, Klebe synthesized high molecular weight polyamine from α,α' -dichloro-*p*-xylene and *N,N'*-bis(trimethylsilyl)piperazine.⁵ Hence, amines **2a** and **3a** were silylated in order to obtain a polymer with high inherent viscosity. Contrary to our expectation, the inherent viscosity of the polyamine obtained by *N*-trimethylsilyl-substituted derivatives **2b**

**Figure 1.** Effect of reaction temperature on the inherent viscosity of polyamine **4** formed by the polycondensation of **1** with **3a** in NMP for 24 h.**Figure 2.** Time dependence of inherent viscosity of polyamine **4** formed by the polycondensation of **1** with **3a** in NMP at 75°C.

and **3b** was less than that of the polymer from the parent amines.

Next, α,α' -dianilino-*p*-xylene (**3a**) was chosen to study the effects of reaction medium, acid acceptor, reaction temperature, and reaction time on the inherent viscosity of the polyamine. Table II shows the influence of reaction medium on the polycondensation. Only in NMP and anisole did the polymerization progress homogeneously, whereas in *N,N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), HMPA, and nitrobenzene the reaction proceeded heterogeneously or changed from homogeneous to heterogeneous during polymerization. Polar aprotic solvents such as DMAc, NMP, and DMSO gave the polyamine with inherent viscosity above 0.2 dl g⁻¹. Anisole, in spite of the homogeneity of the reaction mixture, failed to yield the

polymer with high viscosity. Thus, NMP was chosen as the reaction medium for further studies.

The effect of inorganic acid acceptors was studied in NMP at 150°C (Table III). In general, the bicarbonates gave a polymer with higher inherent viscosity compared with the carbonates. Alkali metal species did not influence the inherent viscosity.

Figure 1 shows the effect of reaction temperature on the polymerization in NMP. The inherent viscosity markedly increased with reaction temperature. The progress of the polycondensation was followed as a function of time by measurement of inherent viscosity of the polymer (Figure 2). The polymerization proceeded fairly rapidly and was almost complete within 1 h at 75°C.

Polymer Characterization

The structure of the polymer thus obtained was confirmed to be *N*-phenylated polyamine by means of IR and NMR spectroscopy and elemental analysis. The IR spectrum of the polymer showed absorptions at 2920 cm^{-1} and 1495 cm^{-1} due to aromatic ring, and no N-H stretching absorption near 3300 cm^{-1} . The ^1H NMR spectrum had signals at 4.6 ppm (4H; methylene protons) and at 7.2 ppm (9H; aromatic protons). The elemental analysis values corresponded well with the calculated values for the proposed structure, as given in the experimental section.

The GPC study of the polyamine with an inherent viscosity of 0.30 dl g^{-1} showed \bar{M}_w and \bar{M}_n of 8550 and 6200, respectively, relative to standard polystyrene.

The *N*-phenylated polyamine was amorphous as indicated by X-ray diffraction. The polymer was soluble at room temperature in chloroform and *sym*-tetrachloroethane, and on heating in DMAc, NMP, DMSO, tetrahydrofuran, and dioxane.

The thermal behavior was evaluated by DTA, TG, and TMA. The glass transition temperature of the polyamine was determined

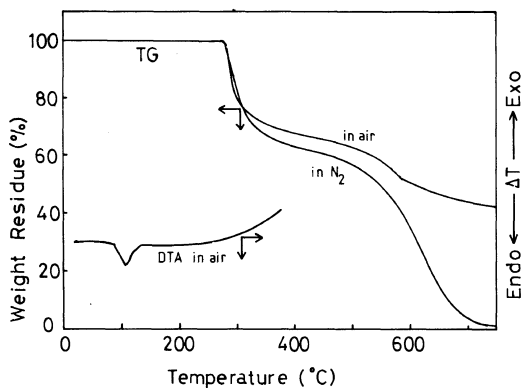


Figure 3. DTA and TG curves of polyamine 4 at a heating rate of 10°C min^{-1} .

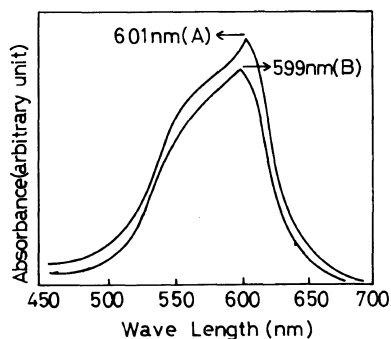


Figure 4. UV spectra of Crystal Violet (A) and violet-colored polymer 5 (B) in NMP solution.

to be 110°C (by DTA) and 120°C (by TMA). Figure 3 shows the DTA and TG curves of the polymer. The polyamine was stable up to 280°C in air and under nitrogen atmosphere.

Polymer Reactions

It is well known that the reaction of *N,N*-dimethylaniline with 4,4'-bis(dimethylamino)benzophenone (BMABP) in the presence of phosphoryl chloride yields Crystal Violet.¹³ Since the *N*-phenylated polyamine synthesized had a structure similar to *N,N*-dimethylaniline, it was of interest to study the reactivity of pendant *N*-phenyl groups of the polyamine toward BMABP. When the polymer in dioxane solution was treated with BMABP and phosphoryl chloride under reflux conditions, the reaction mixture yielded a violet-colored polymer 5 (eq 3).

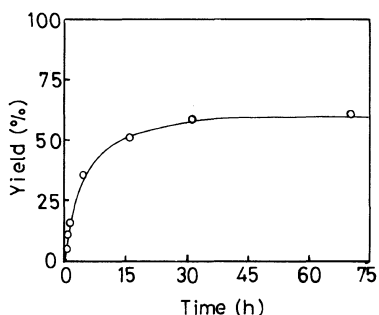
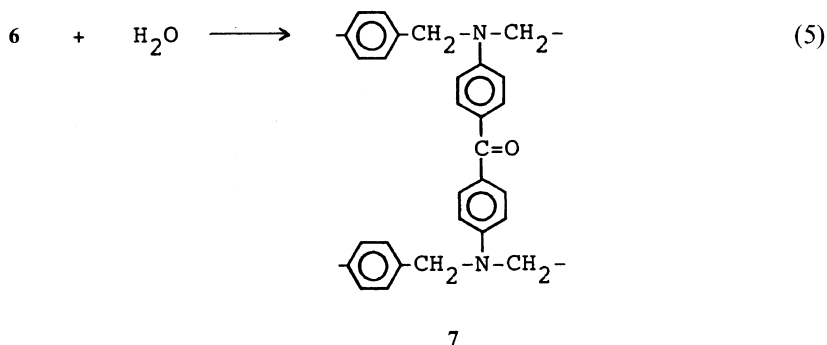


Figure 5. Effect of UV exposure time on the yield of precipitated polymer **6** in dioxane solution.

It was also observed that the IR spectrum of

the crosslinked polymer exhibited a weak carbonyl absorption at 1685 cm^{-1} . This may be due to the presence of small amounts of the proposed benzophenone structure **7** presumably arising from the hydrolysis of **6** during the treatment (eq 5). The TG measurement showed that the crosslinked polymer had an initial decomposition temperature of 140°C in air, which is markedly lower than that of the parent polyamine. The low decomposition temperature in spite of the crosslinked structure may be explained based on the presence of thermally vulnerable bromine in polymer **6**.



In conclusion, the *N*-phenylated polyamine prepared from α,α' -dibromo-*p*-xylene and aniline and its derivatives was highly reactive toward BMABP in the presence of phosphoryl chloride and toward carbon tetrabromide under UV light irradiation, giving a violet-colored polymer and an insoluble product, respectively. Thus, the *N*-phenylated polyamine may be used as a thermally stable polymeric pigment and as a negative-type resist material.

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