Preparation and Properties of Aromatic Polyamide Homologs Containing Chlorine Substituents

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ABSTRACT: In order to study systematically the effect of halogen substituents on both the solubility and the thermal stability of aromatic polyamides, new diamine monomers have been synthesized by introducing chlorine groups onto various positions of 4,4′-diaminobenzanilide for the preparation of chlorinated aromatic polyamides. The monochlorinated aromatic polyamides, i.e., P-LCl and P-RCl, exhibited liquid crystalline property in 100% sulfuric acid solution in the temperature range from 40 and 60°C. However, the dichlorinated sample, i.e. P-LRCl, did not exhibit the liquid crystalline property due to the bulkiness of two chlorine groups. Both P-LCl and P-RCl exhibited unimodal decomposition behavior in contrast to the chlorinated poly(p-phenylene terephthalamide) (PPTA) that has been known to show bimodal decomposition behavior. The decomposition onset temperature of both P-LCl and P-RCl was 567°C, which was higher than 549°C of unchlorinated polyamide, P-NCl, but the same as that of PPTA. The char yield was about 50% for both P-LCl and P-RCl and higher than 40% of both PPTA and P-NCl. In the case of P-LRCl, the decomposition onset temperature was 480°C, but the highest char yield of 60% was obtained. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1387–1392, 2000

Key words: chlorinated aromatic polyamides; P-LCl; P-RCl; P-LRCl; liquid crystalline; unimodal decomposition; high char yield

INTRODUCTION

One of the problems involved in making films based on poly(p-phenylene terephthalamide) (PPTA) is that the corresponding polymers of high molecular weight are difficult to dissolve in any organic solvents and thus strong inorganic acids such as sulfuric acid must be used as a solvent. Chemical modifications of PPTA molecule have thus been considered as plausible methods of improving the polymer solubility.[1–10] Indeed, Toray Industries, Inc., developed an aromatic polyamide film having a PPTA backbone with various substituent groups.[11–13] But thermal properties of the film were not satisfactory owing to the comonomers or substituents introduced. Numerous efforts have been expended to improve the thermal stability, especially the flammability of wholly aromatic polyamides.[14–19] For example, Chaudhuri et al.[10] have considered the correlation between the substituent effect of aromatic polyamides and the flammability.

The introduction of halogen groups onto the aromatic nucleus of a para-oriented aromatic

polyamide has been suggested as a possible method capable of improving both solubility and inflammability of the resultant polymer products.[20–24] However, it has been indicated that the halogenated PPTA exhibits lower thermal stability due to two-step decomposition behavior to yield lower char residue.[14–16,18]

In this study, in order to study systematically the effect of halogen substituents on both the solubility and the thermal stability, new diamine monomers have been synthesized by introducing chlorine groups onto various positions of 4,4′-diaminobenzanilide for the preparation of chlorinated aromatic polyamides.

EXPERIMENTAL

Chemicals

Dimethylacetamide (DMAc), benzoyl chloride, lithium chloride (LiCl), terephthaloyl chloride, N-methyl-2-pyrrolidone (NMP), and pyridine were used after proper purification details of which have been described elsewhere.[25–28]

### Synthesis of Diaminobenzanilide Monomers Having a Chlorine Group

Various diaminobenzanilide monomers having chlorine group were synthesized according to synthetic Scheme 1.

4,4′-Dinitro-2′-Chlorobenzanilide (II)

The amount of 40.76 g (0.29 mol) benzoyl chloride was added to 400 mL DMAc containing 50 g (0.29 mol) of 2-chloro-4-nitroaniline and 60 mL of pyridine. After stirring for 12 h, the solution was poured into water, and the resultant precipitate was washed with distilled water, followed by drying, to get the product of 85.7 g (yield 92%). Other dinitro ompounds (III–V) were similarly synthesized.

4,4′-Diamino-2′-Chlorobenzanilide (VI)

The amount of 20 g 4,4′-dinitro-2′-chlorobenzanilide and 1 g of palladized charcoal (10%) were added in 250 mL of ethanol and then reduced at 80–90°C for 8 h in an autoclave under the H_2 pressure of 20 kg/cm^2. After filtration, the product was dissolved in DMAc to filter out the catalyst. By evaporating DMAc, the crude product of 14.2 g (yield 87.3%) was obtained, which was then pre-
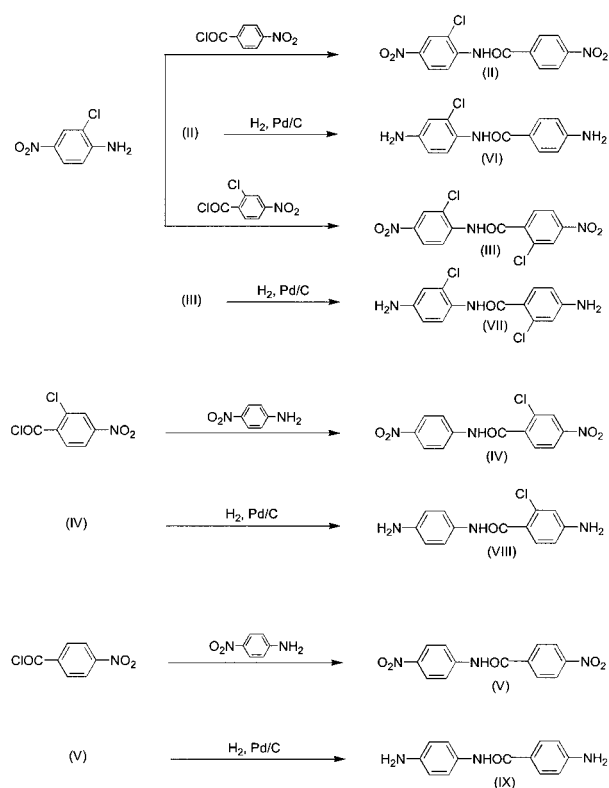
Scheme 1   Synthetic route of 4,4′-diaminobenzanilide having a chlorine group.

cipitated in distilled water. The precipitate became a clear solution of pH 1–2 by adding HCl. The clear solution was filtered and treated on activated carbons in order to decolorize. A further addition of HCl to the filtered solution precipitated the HCl salt that was filtered, dissolved again in water, and neutralized with Na_2CO_3 solution until a new precipitate formed. The product was vacuum dried after enough washing to make the precipitate neutral. Other diamine monomers (VII–IX) having a chlorine group were obtained in a similar manner.

The obtained reaction products were identified from Fourier transform NMR (FTNMR) spectra (see Fig. 1).

Synthesis of Aromatic Polyamides Having Chlorine Group

The amount of 7.5 mmol diamine monomers having a chlorine group were dissolved in 30 mL of DMAc containing 1.9 mL pyridine and 0.75 g LiCl while being mechanically stirred in a stream of nitrogen at room temperature. With vigorous stir-
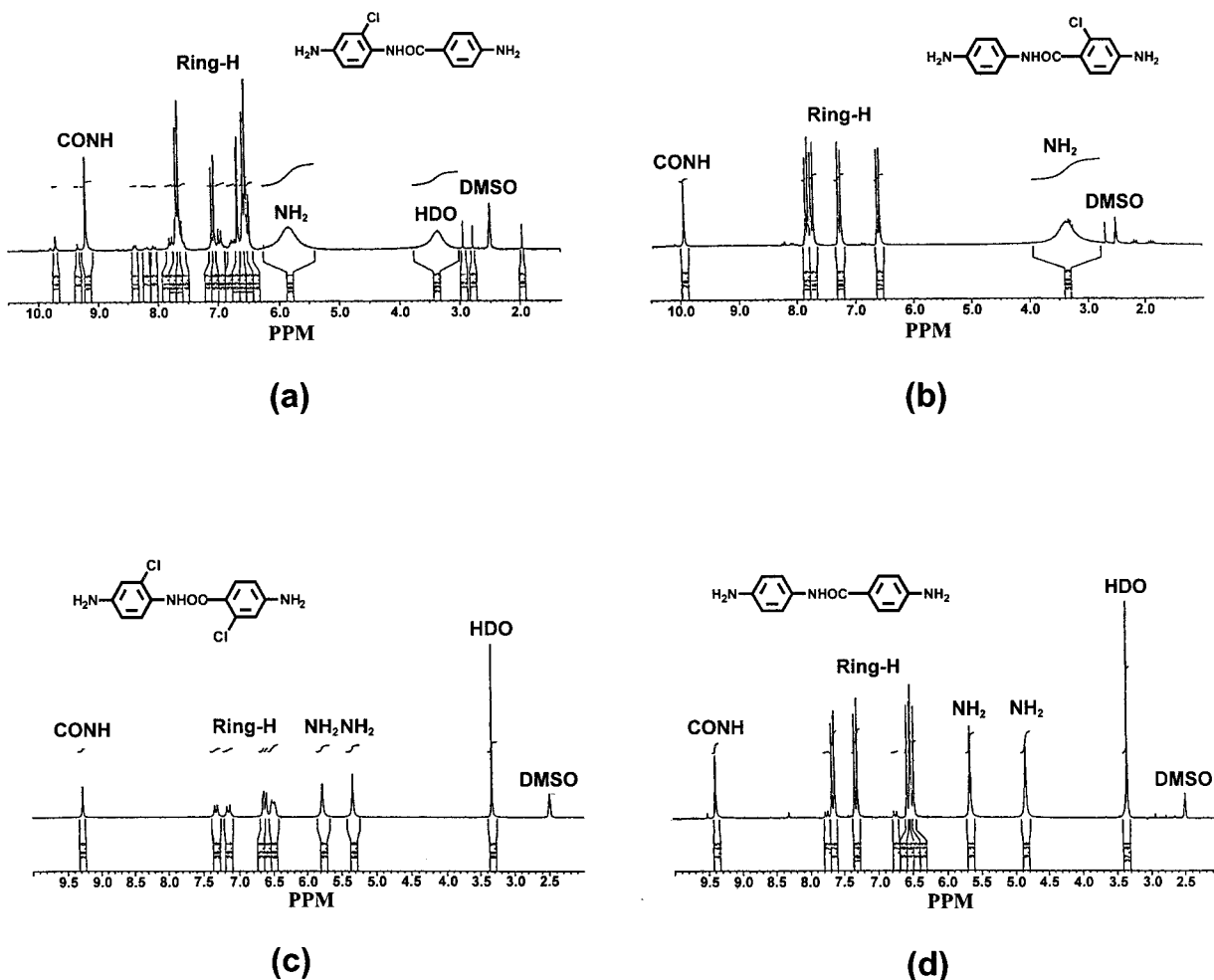
Figure 1 NMR spectra of (a) 4,4′-diamino-2′-chlorobenzanilide, (b) 4,4′-diamino-2-chlorobenzanilide, (c) 4,4′-diamino-2,2′-dichlorobenzanilide, and (d) 4,4′-diaminobenzanilide.

ring, 7.5 mmol of powdered terephthaloyl chloride was added at once at 18–20°C. The solution became extremely viscous after 10 min, which was then poured into water to get the polymer precipitates, followed by washing several times.

Characterization

NMR spectra of synthesized monomers and resultant polymers have been recorded at room temperature on a Bruker FTNMR (200 MHz) spectrometer using DMSO-d_6 or CDCl$_3$ as solvents and tetramethylsilane as an internal standard. The Perkin Elmer FTIR spectrometer 1760X has been complementary used to identify the synthesized monomers.
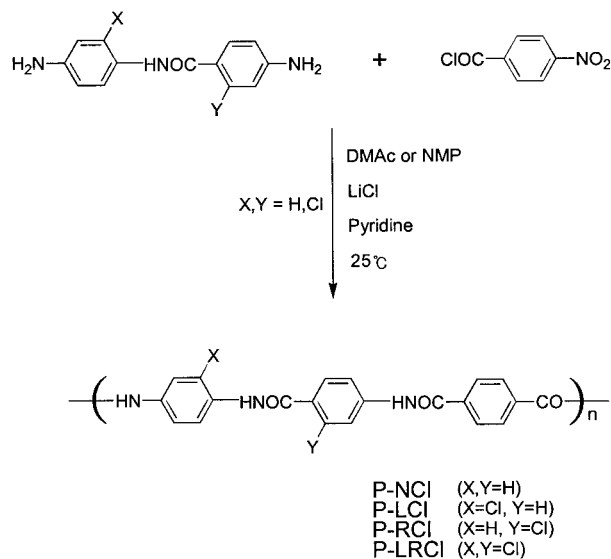
The inherent viscosities of the chlorinated aromatic polyamides were measured with an Ub-

belohde viscometer at 30°C in DMAc at the concentration of 0.5 g/100 mL. Thermal analysis was performed using the Perkin Elmer differential scanning calorimeter Model TGA7 with a scan rate of 20°C/min under nitrogen atmosphere. The Perkin Elmer thermogravimetric analyzer Model TGA7 was also used for the measurement of thermal degradation with a scan rate of 10°C/min under nitrogen atmosphere.

RESULTS AND DISCUSSION

Polymerization Behavior and Liquid Crystalline Properties

Scheme 2 shows the synthetic route to the aromatic polyamides with the chlorine group, and

Scheme 2 Synthetic route of aromatic polyamides having chlorine substituent(s).

Figure 2 TGA thermograms of (a) P-LRCl, (b) P-LCl, (c) P-RCl, (d) P-NCl, and (e) PPTA.

Table I lists the inherent viscosities of those polyamides.

It is interesting to note that the viscosity of aromatic polyamide without the chlorine group is the highest at the monomer concentration of 7 wt %, whereas that of the chlorinated aromatic polyamides increases with the increase of monomer concentration to 12 wt %. Both PPTA and P-NCl precipitates after polymerization whereas the chlorinated polyamides remains in the state of viscose solution due to bulky substituents.

When the polymer solutions with 20% solid contents of P-LCl and P-RCl in 100% sulfuric acid is examined under polorizing microscope with the crossed polars, anisotropic structure formed at

the initial stage started to change at around 40°C and disappeared completely at around 60°C to form an isotropic structure. And P-LRCl does not exhibit the liquid crystalline property due to the bulkiness of two chlorine groups.

Thermal Property

Figure 2 represents TGA thermograms of various chlorinated polyamides and PPTA. A series of studies by Khanna[14–16] have reported that halogenated PPTA, in contrast to the polyamides with other types of substituents exhibits bimodal decomposition behavior, of which degradation mechanism has been proposed by Kapuscinski[18] (Scheme 3).

According to the scheme, the first stage weight loss can be explained by the elimination of HX(X = Cl, Br, etc.) in the reaction between the halogen and neighboring amide bond, and the second

Table I Inherent Viscosity of Chlorinated Polyamides

Polymer	Inherent Viscosity[a]: Monomer Concentration		Polymer Solution
	7 wt %	12 wt %	
PPTA	2.2	1.3	Precipitate
P-NCl	2.5	1.0	Precipitate
P-LCl	2.9	3.2	Solution
P-RCl	2.2	3.9	Gel
P-LRCl	2.0	2.1	Solution

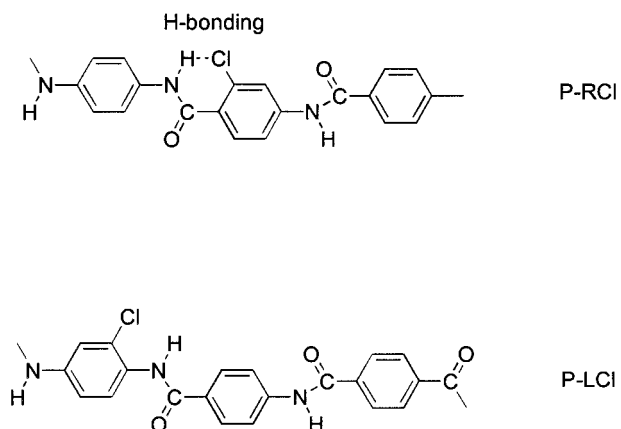[a] Measured at 30°C in DMAc and with 0.5% concentration.
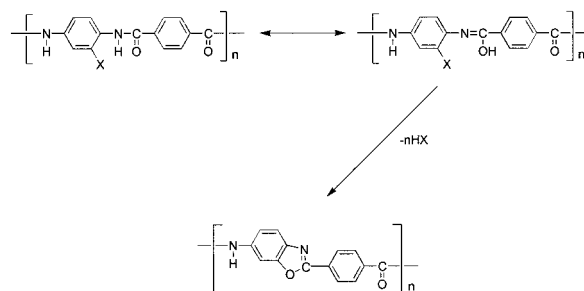
Scheme 3 Possible ring-forming reaction suggested by Kapuscinski.

H-bonding

P-RCl

P-LCl

Scheme 4 Possible intramolecular hydrogen bond in P-RCl.

stage weight loss by the degradation of heterocyclic polymer.

However, both P-LCl and P-RCl, which have a single chlorine group as a substituent, exhibit unimodal decomposition behavior. This strongly indicates that the decomposition mechanism may be different from the above mentioned one, although it is not clear at this stage.

The decomposition onset temperature of both P-LCl and P-RCl is 567°C, which is higher than 549°C of unchlorinated polyamide, P-NCl, but the same as that of PPTA. The char yield is about 50% for both P-LCl and P-RCl and higher than 40% of both PPTA and P-NCl. In the case of P-LRCl, the decomposition onset temperature of 480°C is relatively low, but the highest char yield of 60% is obtained. The reason why P-RCl shows poor thermal stability than P-LCl is that the intramolecular hydrogen bond of P-RCl leads to weakness of interaction of the intermolecular bond (Scheme 4). Similarly, the poor thermal stability of P-LRCl may be due to two chlorine groups which have lower intermolecular order.

CONCLUSIONS

The homologs of aromatic polyamides with chlorine substituents on various positions of 4,4′-diaminobenzanilide unit were synthesized in order to study systematically the effect of the substituents on both the solubility and the thermal stability. All of the chlorinated aromatic polyamides were soluble in the solvents such as DMAc, NMP, etc. In particular, the monochlorinated aromatic

polyamides, i.e., P-LCl and P-RCl, exhibited liquid crystalline property in 100% sulfuric acid solution in the temperature range from 40 and 60°C. However, the dichlorinated sample, i.e., P-LRCl, did not exhibit the liquid crystalline property due to the bulkiness of two chlorine groups. Both P-LCl and P-RCl exhibited unimodal decomposition behavior, which contrasts with PPTA that has been known to show bimodal decomposition behavior. The decomposition onset temperature of both P-LCl and P-RCl was 567°C, which was higher than 549°C of unchlorinated polyamide, P-NCl, but the same as that of PPTA. The char yield was about 50% for both P-LCl and P-RCl and higher than 40% of both PPTA and P-NCl. In the case of P-LRCl, the decomposition onset temperature was 480°C, but the highest char yield of 60% was obtained.

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