# N-Allylated Aromatic Polyamides[†]

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ABSTRACT: Poor processability of poly(*p*-phenyleneterephthalamide) (PPTA) has been a limiting factor for the wider use of this polymer. One approach to improve its processability is to modify the polymer into an N-alkylated or N-arylated tertiary polyamide form. The validity of this approach was studied. A PPTA anion solution was prepared in DMSO with various bases, such as sodium dimsyl, potassium *tert*-butoxide, sodium amide, and lithium dialkylamides. The anion reacts with allyl bromide to give a near quantitative conversion to N-allylated PPTA. This polymer shows no crystallinity and a high solubility in chlorinated solvents. Other N-allylated aramids, such as poly(*m*-phenyleneisophthalamide) (PMIA) and poly(4,4'-biphenyleneisophthalamide) (PPBA), also show totally different properties from the parent polymers. The X-ray structure of $N^1$,$N^4$-bisallylated $N^1$,$N^4$-dibenzoyl(1,4-phenylenediamine) reveals that the torsion angle between two adjacent aromatic rings is much higher than that of the parent secondary amide. This structure suggests that N-allylated PPTA should have a random-coil structure.

## Introduction

Limited processability of rigid-rod aromatic polyamides has triggered various modifications of these polymers into fusible and/or soluble analogues. Substitution on the aromatic rings and utilization of comonomers that have bent structures have been found to improve processability.[1] Whereas those approaches still preserve secondary amide groups, other approaches, such as N-alkylation or N-arylation of the amide groups, which eliminate the interchain hydrogen bonding, also have been sought.[2] In particular, Takanayaki et al. reported a method of N-alkylation via the polyanion of poly(*p*-phenyleneterephthalamide) (PPTA) in DMSO by reacting the polymer with sodium methylsulfinyl carbanion (dimsyl) in DMSO.[3] This method was found to be useful for modification of not only PPTA[4] but also other aromatic amide polymers, such as ring-chlorinated PPTA.[5] However, such modification could affect the geometry of the amide bond conformation, so that the polymer backbone may no longer have a rigid-rodlike structure. We attempted to elucidate the effect of N-alkylation on the structural change of aromatic polyamides.

## Results and Discussion

We decided to investigate the allylated product in depth, because allyl bromide is an excellent electrophile and its vinyl group provides opportunity for further modification of the polymer. Synthesis and thermal cross-linking of N-allylated PPTA was previously reported by Ishizawa et al.[6]

**N-Allylated Aromatic Polyamides.** We reported recently that addition of a judicious amount of a protic solvent lowers the viscosity of the PPTA polyanion solution and allows more concentrated solutions than sodium dimsyl alone.[7] Polyanions of PPTA, poly(*m*-phenyleneisophthalamide) (PMIA), and poly(4,4'-biphenyleneisophthalamide) (PPBA) were prepared as reported. However, in the presence of certain nucleophilic modifiers, such as water and methanol, the allylation did not take place in quantitative yields. As we have proposed earlier,[7] this finding might be due to the bianionic nature of the complex between the polyanion and the hydrogen donor. Under such situations, a competitive substitution reaction between two nucleophiles toward alkylating agents is possible (Chart I). The reaction by pathway A will give alkylated polyamide, but pathway B will give an ether and the polyamide. In order to avoid the undesired reaction pathway, a nonnucleophilic modifier had to be employed. Two approaches have been found to be adequate to obtain a high yield of allylation. One method is to use potassium *tert*-butoxide as a base without any modifier. After deprotonation of the amide group, 1 equiv of nonnucleophilic *tert*-butyl alcohol is generated as an in situ modifier. By this method, 3 and 19 wt % of PPTA and PMIA polyanion solutions were obtained. The polyanion prepared by using $NaNH_2$ also gave a good yield of allylation. Another method involves use of a base with a modifier that has good hydrogen donor properties but is not labile. Carboxamides are known to be good hydrogen bond donors;[8] their p$K_a$'s are lower than that of the polyamides.[7,9] Addition of 2 equiv of formamide and benzamide to the mixture of a base and PPTA in DMSO improved the polyanion formation rate greatly. The effect on dissolution was most profound when a Li base was used. Since the Li salt of the polyanion is not very soluble in DMSO, a homogeneous solution of PPTA cannot be made easily. The mixture of PPTA and lithium dimethylamide or diisopropylamide (LDA) gave a suspension of orange particles even after a long reaction time.[7] Upon addition of a carboxamide, a homogeneous red solution of PPTA anion was instantaneously obtained, which underwent quantitative allylation. The role of these carboxamides is purely that of hydrogen bond donor. If formamide and LDA are premixed in DMSO, an insoluble gelatinous Li salt of formamide is formed. The proton NMR of this mixture indicates that this is a mixture of *N*-lithium formamide and the corresponding amine. Since the p$K_a$'s of carboxamides are less than those of PPTA, this mixture could not form an anionic solution. To our surprise, acetamide did not have any effect on the dissolution of the polyanion.

Upon addition of allyl bromide to the PPTA anion solution, the solution viscosity dropped instantaneously and the color turned orange. The polymer showed good solubility in DMSO and usually remained in solution throughout the reaction. However, from a concentrated solution, the polymer could precipitate out of DMSO during the allylation. The polymer was precipitated from

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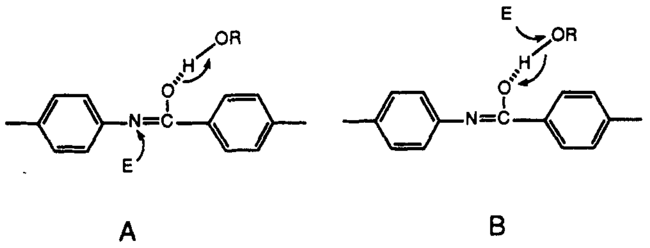
**Chart I**



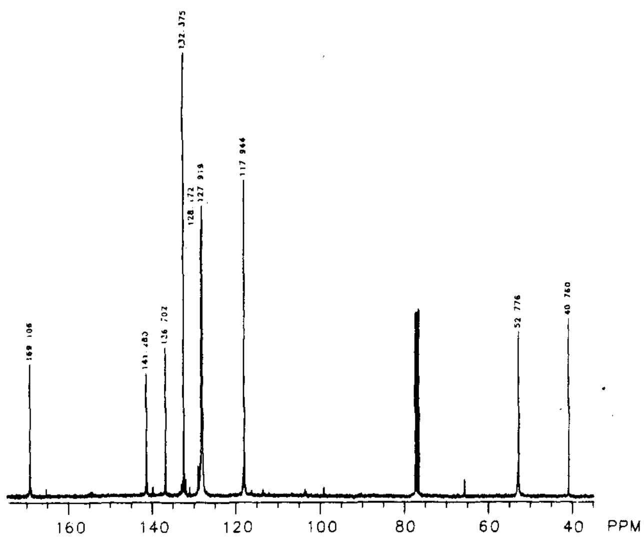


**Figure 1.** $^{13}$C NMR of *N*-allyl-PPTA at 75.6 MHz. The peak at 40.76 ppm is due to DMSO. See the Experimental Section for tentative peak assignments.

water and purified by reprecipitating a THF or $CH_2Cl_2$ solution into petroleum ether. The polymer is very soluble in chlorinated solvents, giving a more than 50 wt % solution in $CH_2Cl_2$. It is not soluble in diethyl ether or toluene. Proton NMR and IR spectra are in accordance with those reported[6] and indicate that mostly N-alkylation had occurred. The proton NMR integration and the absence of an amide II peak at 1540 cm$^{-1}$ in the IR suggest complete allylation. The $^{13}$C NMR of the polymer also confirms exclusive N-allylation, and no O-alkylation, with a single carbonyl carbon peak at 169.1 ppm (Figure 1). PMIA anion similarly prepared also reacted with allyl bromide with heat liberation to give *N*-allyl-PMIA. This material is slightly soluble in THF but insoluble in chlorinated and other common organic solvents. N-Allylated PPBA is soluble in hot chlorinated solvents.

Partially allylated polymers can be prepared by adding less than 1 equiv of allyl bromide to the anion solution or by using nucleophilic modifiers, such as MeOH or water. Partially allylated PPTAs are insoluble in $CH_2Cl_2$ even when about 75% amide has been alkylated. The degree of allylation by the former method, as estimated from IR, corresponds well with the mole ratio of allyl bromide added. The effect of modifiers to the degree of allylation has not been further investigated.

A TGA analysis of *N*-allyl-PPTA shows the onset of weight loss at 410 °C, while DSC shows a broad endotherm at 271 °C. A small exotherm was observed at 222 °C. The polymer visually melted at 280 °C but turned into an infusible yellow material in less than 1 min at this temperature. A fiber, which was drawn from the melt, shows no crystallinity by X-ray diffraction. Partially allylated PPTA does not melt before decomposition, but *N*-allyl-PMIA shows a $T_g$ at 139.5 °C and *N*-allyl-PPBA does not show any thermal activities up to 350 °C. A film cast from a 30% solution of *N*-allyl-PPTA in tetrachloroethane was transparent yellow but very brittle. These findings indicate *N*-allylpolyamides have lost the good mechanical properties that the parent polymers possess. We chose a small molecule to study the structure–property correlation of N-alkylated polyamide.

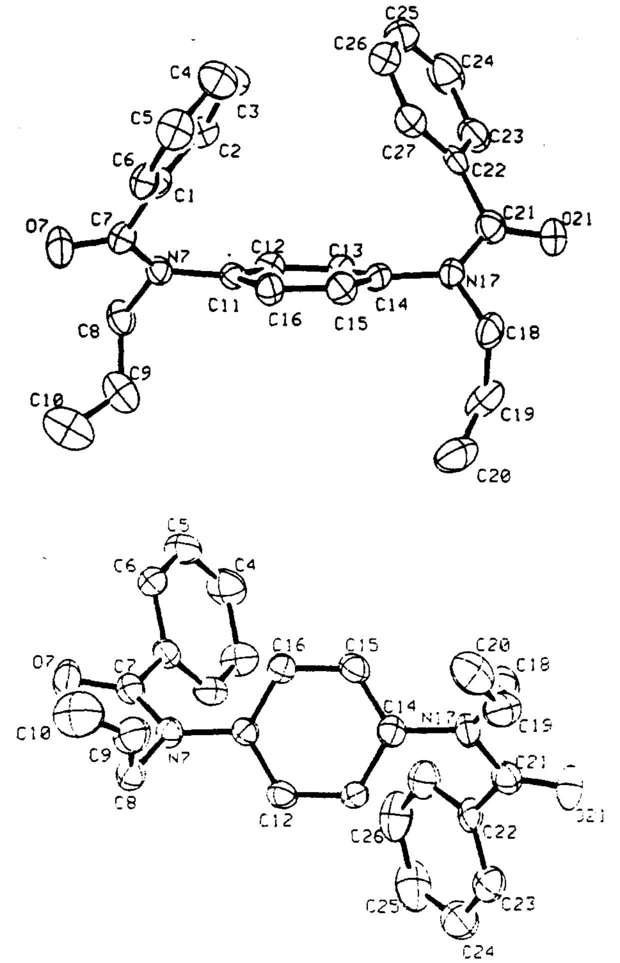


**Figure 2.** Crystal structure of N$^1$,N$^4$-bisallylated *N*$^1$,*N*$^4$-dibenzoyl(1,4-phenylenediamine). The upper structure shows a side view, and the bottom structure projects a top view.

**Model Compound for X-ray Structure Determination.** *N*$^1$,*N*$^4$-Dibenzoyl(1,4-phenylendiamine) (I) was employed as a model compound. The anion of I was obtained in DMSO with potassium *tert*-butoxide or in THF with NaH. Compound I was insoluble in both solvents but reacted with the base in DMSO to give a clear orange solution. In THF, the white powdery anion salt was obtained. The potassium salt of this material also showed a similar trend.[7] Treating the anions of I in either solvent with allyl bromide gave good yields of N$^1$,N$^4$-bisallylated I (II). The spectroscopic data for II confirm the assigned structure. A single crystal of II was obtained from a mixture of $CH_2Cl_2$ and hexane for structure determination.

The structure of II was determined by X-ray diffraction and is shown in Figure 2. The partial double-bond character of the amide bond is confirmed by the bond length of N7–C11 of 1.36 Å. However, the torsion angle of the plane connecting the ortho and ipso carbon of the center ring and the nitrogen and carbonyl carbon (C13–C14–N17–C21 in the Figure 2) is large at 40°. Thus, the two benzoyl groups are distorted from the main axis and placed syn in relation to the central ring (syn isomer). The torsion angle of I along these bonds is close to 0°,[9] which is similar to that of PPTA determined by X-ray diffrac-

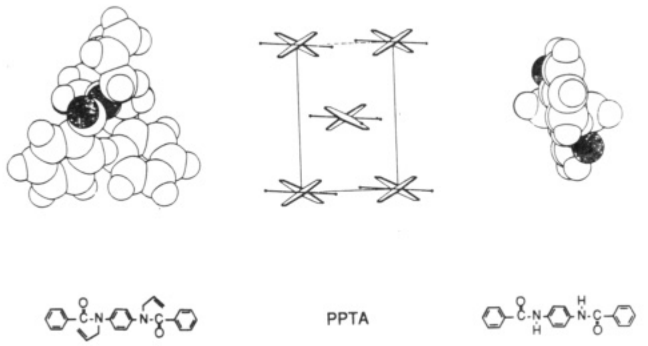


**Figure 3.** Comparison of PPTA and oligomer structure. The example of PPTA packing structure is of "form I".[12] See the similarity between PPTA and compound I in the stacking of the aromatic rings, whereas the rings of compound II are out of alignment.

**Table I**
**Solubility of *N*-Allylpolyamide**

| polymer | solubility $CH_2Cl_2$ | THF | toluene | DMSO |
|---|---|---|---|---|
| *N*-allyl-PPTA | ++ | + | − | + |
| *N*-allyl-PMIA | − | + | − | − |
| *N*-allyl-PPBA | ++ | + | − | + |

**Table II**
**Selected Amido Group Torsional Angles (in deg)**

| bond | crystal structure | syn calcd | anti calcd |
|---|---|---|---|
| C1–C7–N7–C11 | 20.98 | 13.27 | 12.43 |
| O7–C7–N7–C11 | 160.08 | 170.71 | 171.21 |
| C1–C7–N7–C8 | 172.56 | 165.97 | 167.36 |

tion.[11] Such a large torsion angle would reduce the extended chain orientation of the polymer, which plays an important role in determining the physical properties of PPTA. Figure 3 shows a comparison of the structures of I and II with the structure of PPTA projected along the fiber axis. The similarity between the torsion angle of compound I and PPTA can be readily seen. The large torsion angle of compound II distorts the arrangement of the aromatic rings, which forbids the rodlike conformation of the polymer. Crystallinity observed with other N-substituted PPTA[2b,3] must have been due to the side-chain crystallization, since the backbone of the polymer no longer could have the rigid structure. The syn structure of N-alkylated aromatic amide was found from the X-ray structure of *N*-methylbenzanilide. Ab initio calculation with a minimum base set showed that the cis isomer is 3.12 kcal/mol more stable than the trans isomer.[13] AM1 calculation of II showed that the syn isomer is only 0.1 kcal/mol more stable than the anti isomer. However, since the calculated structure of the syn isomer shows some distortion from the crystalline structure (see Table II), the accuracy of the molecular orbital calculations using the empirical set could be low. The syn isomer is probably somewhat more stable than the anti in both solid state and solution. In the case of N-methylated derivatives of 2-[4-(methylamino)phenyl]ethylamine and adipic acid, there are significant differences in the preferences of the amide group conformation of polymeric and oligomeric substances.[14] Nevertheless, a computer simulation of *N*-allyl-PPTA, using a random distribution of syn and anti conformations of II in the ratio of 1 to 0.85 as the repeating units, revealed a random-coil structure.

## Conclusions

N-Alkylation of aromatic polyamides causes loss of desirable physical properties. We have illustrated that this drastic effect originates from changes in the amide bond conformation after alkylation. Alkylation causes large deviation in the torsion angle around the amide group, so that the polymer backbone can no longer have a rigid-rodlike structure.[15]

## Experimental Section

**General Procedure.** DMSO was anhydrous grade from Aldrich. THF was distilled from sodium ketyl anion. Allyl bromide, NaH, and potassium *tert*-butoxide were commercial grade and used without further purification. PPTA is Kevlar[16] pulp type, which was dried at 140 °C for 24 h. PMIA was obtained by precipitating an *N,N*-dimethylacetamide solution of Nomex[16] into water, and the precipitate was dried under vacuum. PPBA was a gift from S. Kwolak. Thermal analysis was done with a Du Pont 9100 thermal analyzer using heating rates of 20 °C/min.

**Preparation of *N*-Allyl-PPTA.** To 113.09 g (0.95 mol) of PPTA pulp (inherent viscosity of 5.5 dL/g in $H_2SO_4$) in 2.4 L of DMSO was added 131.75 g (1.17 mol) of potassium *tert*-butoxide at room temperature, and the mixture was stirred for 24 h. Examination of the clear red solution under polarized light microscopy revealed a small amount of unreacted polymer as small fibrils. The reaction was continued another 24 h after adding 800 mL of additional DMSO. To this solution was added 100 mL (1.15 mol) of allyl bromide at room temperature. The viscosity of the solution dropped almost instantaneously, and a clear solution formed. In about 3 h, a yellow very fine precipitate developed. The precipitate was collected on a Celite pad and then washed with water. The product was removed from the top of the Celite pad and recovered by $CH_2Cl_2$ extraction. The filtrate was quenched with water to obtain some more polymer, which was recovered as above. A total of 108.5 g of the product was obtained. The polymer was purified by reprecipitation in petroleum ether from $CH_2Cl_2$ solution. $^1H$ NMR (ppm, $CDCl_3$): 4.4 (b, 2 H, allylic), 5.0 (d, 1 H, anti terminal vinyl), 5.2 (s, 1 H, syn vinyl), 5.8 (m, vinyl), 5.8 (s, 2 H, aromatic connected to N), 7.1 (s, 2 H, aromatic connected to carbonyl). $^{13}C$ NMR (ppm, $CDCl_3$): 52.8 ($CH_2$ of allyl group), 117.9 (terminal vinyl of allyl), 127.9 (C2,3 of diamine ring), 128.2 (C2,3 of diacid ring), 132.4 (vinylidine of allyl group), 136.7 (C1 of diacid ring), 141.3 (C1 of diamine ring), 169.1 (carbonyl). IR ($cm^{-1}$): 3060 (w), 2920 (s), 1640 (vs), 1600 (shoulder), 1510 (vs), 1400 (s), 1380 (s), 1315 (s), 1265 (w), 1225 (w), 955, 930 (d, w), 725 (w).

**Preparation of *N*-Allyl-PMIA.** To 11.91 g (0.10 mol) of PMIA in 100 mL of DMSO was added 13.82 g (0.12 mol) of potassium *tert*-butoxide at room temperature. A yellow solution was obtained after overnight stirring. Upon addition of approximately 2 mL of allyl bromide, the solution became clearer but exhibited a more intense color. A total of 10 mL (0.115 mol) of allyl bromide was added. The internal temperature reached 75 °C, and the polymer started to precipitate. The mixture was poured into water, and the product was filtered and dried under vacuum. $^1H$ NMR (ppm, THF-$d_8$): 4.3 (br, 2 H, allylic), 5.0 (d, 1 H, anti terminal vinyl), 5.1 (s, 1 H, syn vinyl), 5.8 (br, m), 6.6–6.7 (br, d, 1 H), 6.9–7.0 (br, d, 6 H), 7.5 (br, 1 H). IR ($cm^{-1}$): 3080 (w), 2920 (w), 1650 (vs), 1596 (vs), 1488 (s), 1325 (s), 1295 (w), 1206 (w), 930 (w), 708 (w).

**Preparation of *N*-Allyl-PPBA.** To 200 mL of DMSO containing 1.19 g (10 mmol) of PPBA (inherent viscosity of 1.67 dL/g in $H_2SO_4$) was added 1.46 g (13 mmol) of potassium *tert*-butoxide at room temperature. The mixture was stirred for 15 h. To the resulting yellow solution was added 2.0 mL (23 mmol) of allyl bromide. The solution was then poured into water to give a white powdery product. $^1H$ NMR (ppm, $CDCl_3$): 4.4 (br, 2 H, allylic), 5.1 (br, 2 H), 5.7 (br, 1 H), 6.5–8.0 (br, 4 H). IR ($cm^{-1}$): 3080 (w), 2920 (w), 1650 (vs), 1600 (vs), 1528 (w), 1510 (s), 1400 (s), 1372 (s), 1314 (s), 1224 (s), 1179 (w), 845 (w), 760 (w).

**Syntheses of $N^1$,$N^4$-Bisallyl-$N^1$,$N^4$-dibenzoyl(1,4-phenylenediamine) (II).** To 31.64 g (0.1 mol) of I suspended in 100 mL of DMSO was added 27.63 g (0.25 mol) of potassium *tert*-butoxide. The solution turned red initially and then became yellow in about 10 min. The mixture was stirred for 15 h, but some of the starting material remained unreacted. To this was added 50 mL of allyl bromide, which resulted in color loss. After 2 h, the product was isolated by pouring the solution into 500 mL of water. The precipitate was filtered and washed with MeOH. The product II was extracted into MeOH, whereas the starting material remained insoluble. The product was recrystallized from a mixture of $CH_2Cl_2$ and hexane. Yield: 17 g (42%). $^1H$ NMR (ppm, $CDCl_3$): 4.33 (d, $J$ = 6.6 Hz, 2 H, allylic), 4.93 (d, $J$ = 6.9 Hz, 1 H, anti terminal vinyl), 5.10 (s, 1 H, syn vinyl), 5.8 (m, vinyl), 6.75 (s, 1 H, aromatic connected to N), 7.15 (s, 2 H, aromatic connected to carbonyl). IR ($cm^{-1}$): 3080 (w), 2920 (w), 1643 (vs), 1510 (vs), 1445 (w), 1420 (w), 1375 (s), 1315 (w), 1295 (w), 1225 (w), 1120 (w), 920 (w), 845 (w), 790 (w), 720 (w), 700 (s).

**X-ray Method.** A colorless rectangular 0.4 × 0.22 × 0.5 mm single crystal of II was obtained from slow evaporation of a mixture of $CH_2Cl_2$ and hexane. It was monoclinic, $P21/n$ with a unit cell of $a$ = 12.618 (4), $b$ = 13.407 (5), and $c$ = 12.639 (4) Å and $\beta$ = 92.88 (3)°. The density was 1.233 g/mL. Reflection data were collected by using an Enraf-Nonius CAD 4 diffractometer using a graphite monochromator with Mo K$\alpha$ radiation. A total of 5360 nonzero, independent reflections was collected by the $\omega$ scan method with a scan width of 1.2–1.5° $\omega$ at a speed of 1.5–5.0°/min in the range of $3.0° \le 2\theta \le 55.0°$. No absorption correction was made. The structure was solved by the direct method (MULTAN). It was refined by full-matrix least-squares calculations assuming all non-hydrogen atoms had anisotropic thermal motions and hydrogen atoms were fixed.

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**Supplementary Material Available:** X-ray crystal structure analysis of compound II and tables of fractional coordinates and isotropic thermal parameters (Table I), anisotropic thermal parameters (Table II), interatomic distances (Table III), intramolecular angles (Table IV), intermolecular distances (Table V), and amido group torsional angles (Table VI) (4 pages). Ordering information is given on any current masthead page.

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(15) The possibility of thermal N-Claisen rearrangement of the N-allyl group to regenerate the secondary amide group for interchain H bonding was also investigated. *N*-Allyl-PPTA gave only cross-linked polymer of no obvious structure. *N*-Allyl-PMIA also gave mostly cross-linked polymer, but some of the intensity of the IR peak of secondary amide groups has appeared. From the model reactions with II, a five-membered cyclic amide was isolated. For examples of *N*-allylsulfonamide Claisen rearrangement, see: (a) Inada, S.; Kurata, R. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1581. (b) Inada, S.; Kurata, R.; Ishida, T.; Uda, T.; Okazaki, M. *Nippon Kagaku Kaishi* **1978**, 723. (c) Inada, S.; Nagai, K.; Takayanagi, Y.; Okazaki, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 833.

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