

# Preparation of Polyamides Via the Phosphorylation Reaction. II. Modification of Wholly Aromatic Polyamides with Trifunctional Monomers

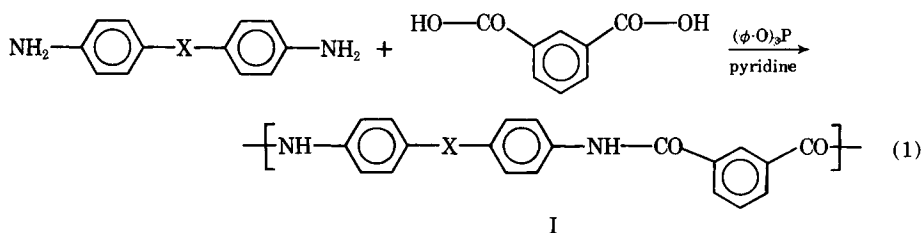
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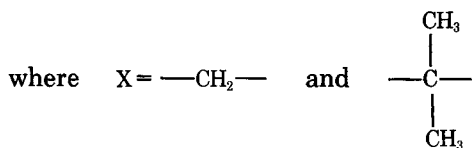
## Synopsis

The trifunctional monomers trimesic acid (TMA) and 3,5-diaminobenzoic acid (DAB), each separately and in combination, were used in amounts of 2 to 5 mole-% in order to increase the molecular weight of aromatic polyamides prepared via the Yamazaki phosphorylation reaction. In general, under comparable conditions the use of DAB led to polymer having higher inherent viscosity (IV) values than did TMA. A typical polymer was the polyisophthalamide of 4,4'-methylenedianiline, MDA-I, prepared by the reaction at 100°C of 4,4'-methylenedianiline (MDA) with isophthalic acid (I) in *N*-methylpyrrolidone (containing 5% dissolved lithium chloride) and employing triphenyl phosphite as condensation agent with pyridine as catalyst. For molar substitutions of 0.0, 2.0, 2.5, and 3.0% of DAB, MDA-I having IV values respectively of 1.1, 1.3, 1.9, and 2.3 was obtained. The latter two samples have IV values in the same range as those obtained for MDA-I prepared from MDA and isophthaloyl chloride in dimethylacetamide (DMAc) via the low-temperature polycondensation method, which prior experience has shown yields polymers that are quite suitable for the spinning of good fibers. At 5 mole-% substitution of DAB, an IV of 3.7 was obtained but a large quantity of gel particles was observed on dissolving the sample in DMAc containing 5% LiCl, indicating that considerable crosslinking had probably occurred. The rod-like polymer poly-*p*-benzamide (PPB) was prepared in similar fashion to MDA-I from *p*-aminobenzoic acid and IV values of respectively 1.6, 2.3, 3.8, and 3.9 were obtained when 0.0, 2.0, 2.5, and 3.0 mole-% of mixed trifunctional monomers were present. A solution of the latter sample dissolved in concentrated sulfuric acid contained considerable gel, indicating that crosslinked polymer was probably produced. It would appear that the chain branching approach for producing high molecular weight PPB for spinning to fibers will not prove useful because PPB having an IV value of about 3 to 4 is considered only marginal for the production of commercial-quality fibers (even though PPB of IV value 1.6 can be spun to high-strength/high-modulus fibers) and because the requisite balance of strength and modulus to elongation to break are only obtained for fibers from PPB having an IV value above about 3.5, and preferably about 5 to 6.

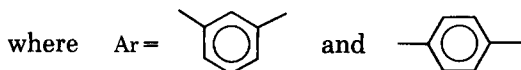
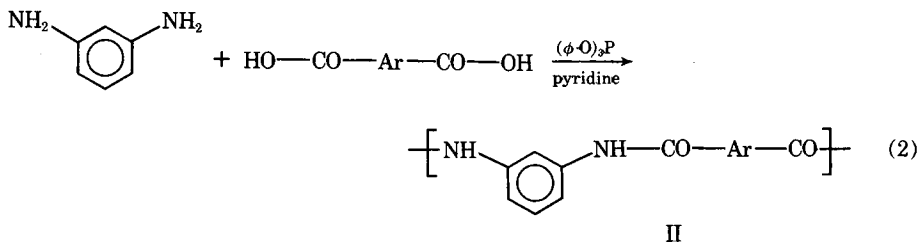
## INTRODUCTION

The phosphorylation reaction has been found to be a very useful laboratory method for the preparation of wholly aromatic polyamides via the polycondensation of aromatic amino acids and the polycondensation of aromatic diacids with aromatic diamines. This reaction has not fulfilled its potential as a commercial route to aromatic polyamides because even under the best conditions found to date, those reported by Yamazaki,<sup>1</sup> polymers of the type exemplified by I have inherent viscosity values limited to about  $1.1 \pm 0.1$  (determined in dimethylacetamide, DMAc, containing dissolved lithium chloride):

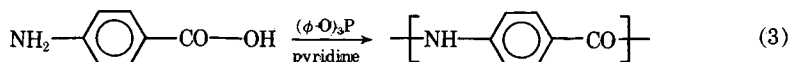




Preston<sup>2</sup> has shown that polymers of the type exemplified by II can be prepared (using the conditions reported by Yamazaki) having inherent viscosity values of  $1.4 \pm 0.1$  (determined in DMAc-5% LiCl):



Rod-like aromatic polyamides, exemplified by poly-*p*-benzamide (PPB),



have been prepared<sup>1,2</sup> having inherent viscosity values, determined in sulfuric acid, up to about 1.7 and, determined<sup>2</sup> in DMAc-5% LiCl, to 3.1. As has been pointed out, the numerically high inherent viscosity values for PPB are not indicative so much of high molecular weight as of the rod-like nature of the polymer chains.<sup>2</sup>

Although it has been shown<sup>2</sup> that polymer of type I ( $X = \text{---CH}_2\text{---}$ ) prepared by the Yamazaki method can be used to prepare fibers of relatively good tensile properties, polymer of inherent viscosity equal to about 1.9 is desired for commercial quality fibers in order to provide fibers that will have good tensile properties under service conditions requiring good flex fatigue resistance, abrasion resistance, etc. Fibers from PPB prepared by the Yamazaki reaction have been reported<sup>2</sup> which have rather high strength and high initial modulus values but have rather low elongation-to-break values as a consequence of the rather low molecular weight polymer used. PPB having an inherent viscosity value of about 3 to 4 is required in order to produce even marginally acceptable commercial-quality fibers. It appears that fibers having the requisite balance of strength and modulus to elongation-to-break, good flex fatigue resistance, etc., are only obtained from PPB having an inherent viscosity value above about 3.5, and preferably about 5 to 6, determined in sulfuric acid.

The work reported here was undertaken with the view in mind of employing the facile Yamazaki phosphorylation reaction to prepare polymers having appreciably higher inherent viscosity values (in the range for commercial-quality

fibers) from PPB and the polyisophthalamide of 4,4'-methylenedianiline, MDA-I. The trifunctional monomers trimesic acid (TMA) and 3,5-diaminobenzoic acid (DAB) were employed to introduce a moderate amount of chain branching into PPB and MDA-I in order to obtain the increase in inherent viscosity values of these polymers. It is understood, of course, that an increase in the inherent viscosity values alone for MDA-I and PPB would not necessarily ensure that fibers of significantly higher tensile properties (or "toughness") would be obtained from these modified polymers.

## RESULTS AND DISCUSSION

### Polymerizations

MDA-I was prepared as described earlier<sup>2</sup> with the exception that 1-5 mole-% of each TMA and DAB was employed in the polycondensation reaction, eq. (1). The stoichiometry of the reaction was maintained as regards total carboxyl groups and amine groups. For example, when TMA was used, the amount of isophthalic acid (IA) was decreased proportionally so that the total IA + TMA acid groups would equal the total amine groups of the 4,4-methylenedianiline (MDA). For DAB, which contains two amine groups and a carboxyl group, the amounts of IA and MDA both were adjusted to give balanced stoichiometry. Mixtures of DAB and TMA were employed to modify MDA-I; suitable adjustments were made in IA and MDA to yield balanced amine and carboxyl groups.

For the polycondensation of *p*-aminobenzoic acid to yield PPB, TMA and DAB were used together to modify the polymer because use of either trifunctional monomer alone produced PPB having lower inherent viscosity values than unmodified polymer, probably because of the imbalance of endgroups.

### Preparation of Modified MDA-I

Use of less than 2.0 mole-% DAB produced MDA-I of inherent viscosity less than that of the control (Table I) and use of less than 3.0 mole-% TMA likewise resulted in MDA-I of lower inherent viscosity than the control. In general, under comparable conditions the use of DAB led to polymer of higher inherent viscosity than did TMA. The polymers from 2.5 to 3.0 mole-% DAB and 3 mole-% TMA have inherent viscosity values in the same range as those obtained for MDA-I prepared from MDA and isophthaloyl chloride in DMAc via the low-temperature polycondensation method, which, prior experience has shown, yields polymers that are quite suitable for the spinning of good fibers. At 5 mole-% substitution of either DAB or TMA, solutions of the polymers in sulfuric acid contain gel particles. A mixture of 1 mole-% each of DAD and TMA produces a polymer having an inherent viscosity value in the desired range.

### Preparation of Modified PPB

Modified PPB which forms gel-free solutions can be produced as long as the total (i.e., DAB + TMA) mole-% substitution does not exceed about 2.5%. Polymer of inherent viscosity 3.8 can be produced (Table II) which is free of gel.

TABLE I  
Modification of MDA-I with Trifunctional Monomers

Trifunctional monomer	Mole-% substitution <sup>a</sup>	Inherent viscosity <sup>b</sup>
None	0.0	1.1
3,5-Diaminobenzoic acid (DAB)	1.0	0.7
	2.0	1.3
	2.5	1.9
	3.0	2.3
	5.0	3.7 <sup>c</sup>
Trimesic acid (TMA)	1.0	0.8
	2.0	0.9
	3.0	2.0
	5.0	2.1
Mixed DAB + TMA (1% DAB, 1% TMA)	2.0	2.0

<sup>a</sup> See section on polymerization for discussion of calculations.

<sup>b</sup> Determined in DMAc-5% LiCl.

<sup>c</sup> Solutions contained gel particles.

TABLE II  
Modification of PPB with Trifunctional Monomers

	Mole % acid monomers <sup>a</sup>		Inherent viscosity <sup>b</sup>
	3,5-Diaminobenzoic	Trimesic	
	0.0	0.0	1.6
	1.5	0.5	2.3
	2.0	0.5	3.8
	2.5	0.5	3.9 <sup>c</sup>
	1.9	0.6	3.8
	0.0	3.0	3.9 <sup>c</sup>

<sup>a</sup> See section on Polymerization for discussion of calculations.

<sup>b</sup> Determined in concentrated sulfuric acid.

<sup>c</sup> Solutions contained considerable amounts of gel particles.

Above 2.5 mole-% total substitution, small to large amounts of gel are produced and the inherent viscosity values are not materially increased. Below a total 2.5 mole-% substitution, the inherent viscosity value is considerably higher than that previously reported via the phosphorylation reaction, but it is still not high enough to be particularly useful for the preparation of fibers having a good balance of tensile properties.

A copolymer of PPB and poly-*m*-benzamide (PMB) was prepared using a 75:25 ratio of *p*-aminobenzoic acid to *m*-aminobenzoic acid. The inherent viscosity value of this polymer was 0.94, i.e., in the same range as for MDA-I and other nonrod-like aromatic polyamides. It is interesting to note that this copolymer has a higher inherent viscosity value than those (0.40 and 0.43) previously reported<sup>1,2</sup> for PMB.

A copolymer of PPB and MDA-I was prepared using 10 mole-% *p*-aminobenzoic acid in the polycondensation reaction; the inherent viscosity value for this copolymer was 0.98, i.e., about the same as for unmodified MDA-I.

### Miscellaneous Modified Polymers

Previous preparations<sup>1,2</sup> of unmodified poly-*p*-phenyleneterephthalamide (PPD-T) via the phosphorylation reaction have yielded polymer having inherent viscosity values of 0.18 and 0.28. An attempt was made to prepare a modified PPD-T which might be more soluble than regular PPD-T because of use of minor amounts of meta-oriented rings. Such a polymer should not be limited in molecular weight because of precipitation during the polycondensation reaction and should have a very high inherent viscosity value reflecting the presence of rod-like chains and the presence of chain branching. A PPD-T copolymer containing 4.5% DAB and 1.5% TMA was prepared having an inherent viscosity of only 0.32 despite the fact that the reaction mixture was ungelled and very little evidence of precipitated polymer was present. Thus, factors other than mere poor solubility appear to be involved in the synthesis of PPD-T via the phosphorylation reaction.

Fibers from aromatic polyamides containing sulfonic acid groups have been reported<sup>3</sup> which have enhanced affinity for basic-type dyes. Thus, 2,4- and 3,5-diaminobenzenesulfonic acids have been copolymerized with *m*-phenylenediamine in a polycondensation with isophthaloyl chloride and the copolymer has been spun to fibers which are claimed<sup>3</sup> to dye to deep shades. A more convenient sulfonic acid source, 5-sulfoisophthalic acid (SIA) was condensed with MDA via the phosphorylation reaction to yield a polymer of inherent viscosity 0.4. (It thus appears likely that the sulfonic acid groups do not take part in the phosphorylation reaction.) Both the free acid and the sodium salt yield similar results for the homopolymer. A copolymer of MDA-I containing 25% SIA units was prepared from the free acid and the sodium salt, yielding polymer having inherent viscosity values of 0.5 and 0.8, respectively. A 1:4 blend of the latter copolymer with MDA-I (obtained from MDA and isophthaloyl chloride) was wet spun to bright fibers of good tensile properties. Such fibers could be dyed to deep shades using basic dyes.

### EXPERIMENTAL

The experimental details for the preparation of the unmodified polyamides were described elsewhere<sup>20</sup>; the polymers of this report were prepared in a similar manner.

### References

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Received October 4, 1978

Revised January 9, 1979