



Short communication:

## Relevance of purification procedures in the direct synthesis of poly(*p*-phenyleneterephthalamide) from its dimer

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**Abstract:** The direct synthesis of poly(*p*-phenyleneterephthalamide) has been successfully performed by polymerizing its dimer, *N*-(4-aminophenyl)terephthalamic acid, instead of *p*-phenylenediamine and terephthaloyl chloride or terephthalic acid, as commonly carried out. An intrinsic viscosity much higher than those typical of the commercial fibres (Kevlar<sup>®</sup>) has been obtained. The procedure and the advantages of the method are highlighted.

### Introduction

For its excellent mechanical and flame resistance properties, poly(*p*-phenylene-terephthalamide), PPDT, is certainly the most important aromatic polyamide [1] and is widely used for those applications in which the above features, joined to low density, are requested. In particular, PPDT is often employed as a steel substitute in the automotive [2], aeronautics and aerospace industries [3] as well as for the preparation of ropes [4], flame retardant textiles, bulletproof garment [5] etc. However, as far as molecular weights (MWs) are concerned, the present commercial products based on PPDT (*i.e.*, Kevlar<sup>®</sup>, Twaron<sup>®</sup>) have not reached yet the optimum values necessary for the attainment of the best physico-mechanical properties of this material. The reasons for these not very high MWs are directly linked to the synthetic approaches in use for their production.

Indeed, the only solvent mixtures able to keep PPDT in homogeneous solution during its synthesis, thus allowing it to progressively reach higher molecular weights, are those based on hexamethylphosphoric triamide (HMPA) and LiCl and/or CaCl<sub>2</sub>. However, HMPA has been recognized as a highly toxic compound and its use in industrial applications discontinued. Consequently, PPDT is now prepared in *N*-methylpyrrolidone (NMP) / LiCl and/or CaCl<sub>2</sub> solvent mixtures. These media are not able to keep PPDT molecularly dissolved but only to highly swell it. For this reason, the macromolecules grow in a quasi-gel state, thus preventing any possibility to

reach the high molecular weights obtained in HMPA solution, which provides the highest values quoted so far. Namely, in HMPA-based media PPDT fibres with intrinsic viscosity,  $[\eta]$ , as high as 22.1 dl/g have been obtained [6], whereas in media constituted of NMP,  $[\eta]$  values equal to 6 - 7 dl/g only are typically found. In both HMPA and NMP systems, the polymerization reaction is industrially performed at 0 to 10°C by allowing terephthaloyl chloride (TCI) and *p*-phenylenediamine (PPD) to react in the presence of a tertiary amine. Because of the high reactivity of TCI, the reaction is instantaneous. However, such high tendency to react with nucleophilic species implies particular care during TCI storage. Besides, PPD has a relevant tendency to oxidize and sublime, thus affecting the requested equimolar ratio between amino and carboxylic groups, which is one of the most relevant parameters to control in order to reach very high molecular weights. Moreover, PPD is considered a toxic compound and precautions are necessary for its handling and use.

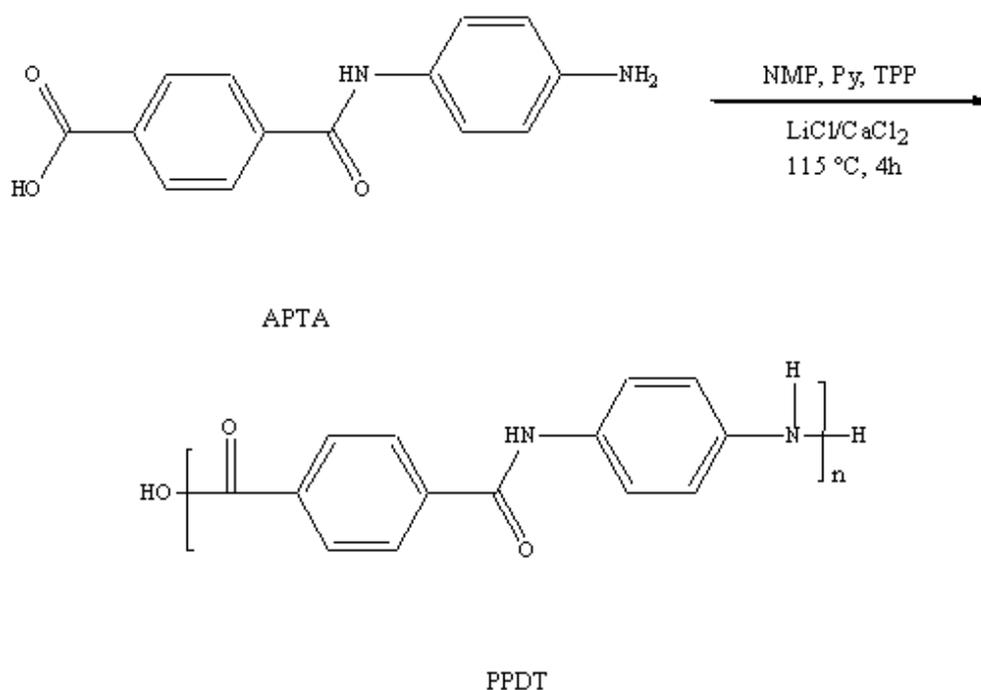
An alternative synthetic approach is represented by the so-called 'direct' synthesis. By this route, aromatic polyamides are prepared by direct reaction of carboxylic acid and amino groups. These polymerizations are carried out at higher temperature (80 - 115°C) and need longer times (2 - 4 h). Triphenyl phosphite (TPP) in large amount is generally used both as the activator of the carboxylic groups and as condensing agent. The above method has the advantage of using a non-activated compound, such as a carboxylic acid, which can be stored for long times and can be handled without particular precautions.

The first studies on the direct synthesis of aramids have been performed by Yamazaki *et al.* [7] in the seventies. For PPDT, the reaction mixture was constituted of terephthalic acid (TA), PPD, NMP, pyridine (Py), LiCl (or CaCl<sub>2</sub>) and TPP. PPDT prepared via this method was characterized by very low molecular weight ( $[\eta] \approx 0.2$  dl/g), because of the very poor solvent power of the medium causing oligomer chains to precipitate before reaching higher degrees of polymerization.

In 1982, Higashi *et al.* [8] found that if LiCl and CaCl<sub>2</sub> are dissolved together in the above solvents, PPDT of  $[\eta]$  as high as 4.5 dl/g can be synthesized. In subsequent years, the method was improved by Preston *et al.* [9] and by our group [10-13]. In particular, we have demonstrated that, by both a thorough set-up of experimental conditions and accurate purification procedures of all reaction components, PPDT characterized by  $[\eta] = 11.0$  dl/g (*i.e.*, a much higher value than those typical of commercial products) can be obtained.

In 1984, Preston *et al.* [14] proposed the use of *N*-(4-aminophenyl)terephthalamic acid (APTA) as starting material for the synthesis of PPDT (Scheme 1). However, PPDT of  $[\eta]$  only equal to 4.3 dl/g was obtained, a value much lower than that reachable using PPD and TCI or TA as starting materials (Tab. 1). To our knowledge, no further improvements have been published so far on the use of APTA in the synthesis of PPDT.

As already mentioned, we have previously published [11,12] on the dramatic influence of extended purification procedures, referred to all reaction components, on the molecular weight of the resulting aramids (*viz.*, PPDT and poly(*p*-benzamide)). We believe that the above influence is very general and can provide a real breakthrough in polycondensation and related reactions. Its relevance, however, has not been fully recognized yet, often causing unjustified limitations in upper values of MW. With the present work we planned to ascertain whether both the purification extent and the procedures employed could increase PPDT molecular weight also when APTA is used.



**Scheme 1.** Direct synthesis of poly(*p*-phenyleneterephthalamide) (PPDT) by polymerization of *N*-(4-aminophenyl)terephthalamic acid (APTA)

**Tab. 1.**  $[\eta]_{\text{PPDT}}$  obtained in the present work and compared with literature values

Sample	Ref.	Reactants or monomer	$[\eta]^a$ in dl/g
1 Kevlar <sup>®</sup> (commercial fibres)	–	TCI + PPD	6 - 7
2 PPDT (Yamazaki et al.)	[7]	TA + PPD	0.2
3 PPDT (Higashi et al.)	[8]	TA + PPD	4.5
4 PPDT (Preston et al.)	[9]	TA + PPD	6.2
5 PPDT (previous work of ours)	[13]	TA + PPD	11.0
6 PPDT (Preston et al.)	[14]	APTA	4.3
7 PPDT	present work	APTA	8.4

<sup>a)</sup> In 96% H<sub>2</sub>SO<sub>4</sub> at 25°C.

## Results and discussion

The intrinsic viscosity of PPDT synthesized from APTA by using highly purified reagents is given in Tab. 1 (entry 7) and compared to the only literature value previously reported for the same monomer by Preston *et al.* [14] (entry 6), as well as to values typical of the corresponding commercial products (entry 1), and to data reported by Yamazaki *et al.* [7], Higashi *et al.* [8], Preston *et al.* [9] and ourselves [13] using PPD and TA as reactants.

As can be seen from the wide range of  $[\eta]$  values given in Tab. 1, PPDT preparation is particularly critical and strongly dependent on the conditions chosen. For instance, as stated above, the simple addition of CaCl<sub>2</sub> to Yamazaki's medium resulted in a

rather large improvement of PPDT intrinsic viscosity (from 0.2 to 4.5 dl/g; entries 2 and 3) and, together with minor differences, was used to define the so-called Higashi medium. Later on, Preston *et al.* have shown that, by carrying out PPDT synthesis in the same Higashi medium but at 115°C instead of 100°C, a further and relevant increase of  $[\eta]$  is obtained up to 6.2 dl/g (entry 4), a value comparable to that of commercial PPDT fibres ( $[\eta] = 6 - 7$  dl/g; entry 1).

Lately, we suggested that direct polyamidation of PPD and TA can lead to additional  $[\eta]$  enhancement, using the same experimental conditions as employed by Preston *et al.* but paying special attention to the purification of all reaction components [10-13]. Namely,  $[\eta]$  as high as 11.0 dl/g has been obtained [13]. This value represents the highest  $[\eta]$  reported so far in literature for PPDT in solvent media not based on HMPA.

As mentioned in the Introduction, both industrial and direct polyamidation systems have some disadvantages related to the use of PPD and TCI or TA. Let us briefly recall them here: difficult storage and handling of TCI because of its high reactivity, in particular with nucleophilic impurities, high toxicity of PPD, and high tendency of PPD to sublime and oxidize, thus affecting reaction stoichiometry.

In general, as already mentioned, the use of strictly equimolar amounts of mutually reacting functional groups is necessary for the achievement of very high molecular weights. For these reasons, an attempt to overcome some of the above drawbacks has been tried by Preston *et al.* [14], who polymerized the dimer APTA by direct polyamidation. However, as mentioned above, the intrinsic viscosity of PPDT reached by his group ( $[\eta] = 4.3$  dl/g) was significantly lower than the values obtained by two-reactant polycondensation. Similarly to what has been previously done for the polycondensation of PPD and TA, we tried to verify whether an extensive purification of the monomer APTA, joined to the use of highly purified other components of the reaction mixture, as described in refs. [11,12], results in an improvement of the method.

It is also worth noting that APTA, having an already formed amido linkage, allows the synthesis of PPDT by using only half of the amount of TPP requested when the polycondensation is carried out from TA and PPD. This fact is particularly advantageous not only for the reduction of both costs and waste production, but also for the reduced formation of phenol, an undesirable by-product which can react (although to a minor extent) with the carboxy end groups, thus limiting chain growth [11].

From the data of Tab. 1 (entry 7), it can be noticed that PPDT characterized by  $[\eta] = 8.4$  dl/g has been obtained. This value doubles that quoted by Preston *et al.* [14] starting from the same monomer, and remains significantly higher than the values typical of the commercial fibres.

On the basis of the above results, it should be underlined that, as a general rule, extensive purification of all reaction components is of fundamental relevance in all polycondensations, regardless of the starting monomer system (either AB or AA, BB). In this respect, we have already shown that PBA characterized by  $[\eta] = 2.38$  dl/g is prepared by polymerizing *p*-aminobenzoic acid (pABA) [12]. The above value, obtained in a highly purified solvent medium, is the highest reported so far for the polymerization of this monomer and can be favourably compared to that previously reported by Preston *et al.* ( $[\eta] = 1.8$  dl/g) [15]. However, it should be mentioned here that in both papers pABA was used as received without any further purification. As a consequence of what has been found in the present work, we suggest reconsidering all polycondensations (both involving AA, BB and AB monomer systems) in order to

verify whether MWs can be further increased by more stringent purification procedures of every reaction component. Indeed, when less purified chemicals were used in the present work, much lower  $[\eta]$  values of PPDT were found (e.g.,  $[\eta] < 1$  dl/g for samples prepared using not perfectly anhydrous  $\text{CaCl}_2$ , etc.). Therefore, we may guess that the intrinsic viscosity value of 8.4 dl/g, being still lower than that found when using PPD+TA in highly purified medium ( $[\eta] = 11.0$  dl/g; entry 5), needs further optimization. In other words, the above synthesis can be still improved by a thorough study on all reaction parameters, including the effects of monomer and TPP concentration, reaction temperature and time, type and amount of dissolved salt(s).

## Experimental part

Intrinsic viscosity measurements were carried out in an Ubbelohde viscometer at 25°C in 96%  $\text{H}_2\text{SO}_4$ .  $^1\text{H}$  NMR spectra were recorded on a Varian Gemini NMR spectrometer at 300 MHz. FT-IR spectra were performed on a Perkin Elmer Spectrum One FTIR. GC-MS analysis was recorded on a GC-Autospec chromatograph.

All reagents and solvents were purchased from Aldrich. Kevlar samples were kindly supplied by E.I. DuPont de Nemours. Monomethyl terephthalate and thionyl chloride were used as received. The other chemicals were purified as indicated below.

All the following operations were performed under argon atmosphere.

NMP was refluxed in vacuum (membrane pump) over  $\text{CaH}_2$  and molecular sieves (4A) for 24 h and afterwards distilled under the same conditions. Then, it was refluxed over  $\text{P}_2\text{O}_5$  and molecular sieves (4A) for 12 h and distilled (this procedure was repeated twice). Tetrahydrofuran (THF) was refluxed over metallic Na for 24 h and distilled. Py was refluxed over NaOH for 24 h and distilled afterwards (this procedure was repeated twice). TPP was twice distilled in vacuum. LiCl and  $\text{CaCl}_2$  were dried at 400°C in vacuum.

### *Monomethyl terephthaloyl chloride (MMTCl)*

A 100 ml round bottom flask, equipped with a reflux condenser and a magnetic stirrer, was loaded with 2 g of monomethyl terephthalate and an excess of thionyl chloride. The reaction mixture was refluxed for 2 h until the excess of thionyl chloride was distilled off and the liquid was allowed to cool. The precipitated MMTCl was isolated by filtration. Yield was quantitative.

### *N-(4-Nitrophenyl)terephthalamic acid methyl ester (NPTAME)*

A 50 ml round bottom flask was loaded with 2.18 g of MMTCl dissolved in 10 ml of anhydrous THF and 2 ml of anhydrous Py. A mixture of 1.53 g of *p*-nitroaniline dissolved in 25 ml of anhydrous THF was added dropwise to the above solution at 0°C. The reaction was carried out at 0°C for 1 h. Then, the mixture was poured into 5% aqueous HCl. The resultant precipitate was collected by filtration, recrystallized three times from *N,N*-dimethylformamide (DMF)/water, washed several times with boiling water and diethyl ether, and dried in a vacuum oven for 24 h at 60°C. Yield: 94%.

$^1\text{H}$  NMR:  $\delta = 11.0$  s (1 H); 8.3 m (2 H); 8.0 m (6 H); 3.9 s (3 H).

### *N-(4-Nitrophenyl)terephthalamic acid (NPTA)*

In a beaker, 1 g of NPTAME was dissolved in 10 ml of hot NMP and, under stirring, 600 ml of 5% aqueous NaOH were slowly added. After 20 min, the reaction was quenched by dropwise addition of concentrated HCl to pH 2. The resultant precipitate was collected by filtration, recrystallized three times from DMF/water, washed several times with boiling water and dried in a vacuum oven for 24 h at 60°C. Yield: 90%.

$^1\text{H NMR}$ :  $\delta$  = 11.0 s (1 H); 8.3 m (2 H); 8.0 m (6 H).

### *N-(4-Aminophenyl)terephthalamic acid (APTA)*

In a 50 ml two-neck round bottom flask equipped with an inlet and outlet for  $\text{H}_2$ , 0.5 g of NPTA was dissolved in 10 ml of anhydrous NMP. After several vacuum-argon cycles, 0.05 g of  $\text{Pd/Al}_2\text{O}_3$  were added to the above solution. The reaction was carried out with stirring for 48 h at room temperature. Then, the mixture was filtered and poured into water. The resulting precipitate was filtered, recrystallized three times from DMF/water, washed several times with boiling water and dried in a vacuum oven for 24 h at 60°C. Yield was quantitative (m.p. > 200°C).

$^1\text{H NMR}$ :  $\delta$  = 10.0 s (1 H); 8.0 m (4 H); 7.4 m (2 H); 6.5 m (2 H).

FT-IR (nujol): 3600, 3300, 2896, 1720, 1463, 1650, 1377, 729, 1306  $\text{cm}^{-1}$ .

MS: molecular peak = 256.

Elemental analysis:	Calc.	C 65.62	H 4.72	N 10.93
	Found	C 65.08	H 4.82	N 10.98

### *Poly(p-phenyleneterephthalamide) (PPDT)*

0.1 g of APTA were dissolved in 4 ml of anhydrous NMP. Afterwards, 0.085 g of anhydrous LiCl and 0.25 g of anhydrous  $\text{CaCl}_2$  were added to the above solution. Several vacuum-argon cycles were performed and 1 ml of Py and 0.11 ml of TPP were added to the solution. The reaction flask was placed in an oil bath set at 115°C. The reaction was carried out at this temperature for 4 h. Afterwards, the reaction mixture was poured into 200 ml of methanol. The precipitated polymer was filtered and extracted in a Soxhlet apparatus for 48 h with boiling methanol. Then, it was dried in a vacuum oven for 24 h at 80°C. Yield was quantitative.

## Conclusions

At this stage of our studies on APTA, we can summarize our results as follows:

i) PPDT characterized by  $[\eta]$  higher than those of commercial products has been prepared; ii) APTA monomer can be used and stored without any precaution necessary for TCI and PPD; iii) most of the problems linked to the maintenance of exact stoichiometry between the reactants AA, BB are avoided, making the polymerizing system (and presumably the features of the resulting material) less sensitive to the relative concentrations of reaction components. Further studies devoted to the evaluation of the most suitable reaction conditions are under way and will be reported in a forthcoming paper.

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