

Role of the reaction parameters in the direct synthesis of aromatic polyamides

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Abstract: A thorough study, devoted to analyzing the role of various reaction parameters in the direct synthesis of poly(*p*-phenylene terephthalamide) and poly(*p*-benzamide), activated by triphenyl phosphite, is described. The effects of temperature, salt type and concentration, amount of triphenyl phosphite and its stepwise introduction, as well as monomer and reagent concentrations, are considered. The inherent viscosity values of the above aromatic polyamides are higher than those reported in the literature for analogous syntheses and are comparable to the values of typical samples obtained by the acyl chloride routes.

Key words: poly(*p*-benzamide), poly(*p*-phenylene terephthalamide), triphenylphosphite, direct synthesis, aromatic polyamides.

Résumé : On décrit une étude complète orientée vers l'analyse du rôle de divers paramètres réactionnels dans la synthèse directe du poly(téréphthalamide de *p*-phénylène) et du poly(*p*-benzamide), activée par le phosphite de triphényle. On a considéré l'effet de la température, du type de sel et de sa concentration, de la quantité de phosphite de triphényle et de son introduction par étape ainsi que des concentrations de monomère et de réactifs. Les valeurs de la viscosité inhérente des polyamides aromatiques mentionnés plus hauts sont plus élevées que celles rapportées dans la littérature pour des synthèses analogues et elles sont comparables aux valeurs d'échantillons typiques obtenus par des voies impliquant les chlorures d'acyles.

Mots clés : poly(*p*-benzamide), poly(téréphthalamide de *p*-phénylène), phosphite de triphényle, synthèse directe, polyamides aromatiques.

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Introduction

In 1974, Yamazaki et al. (1) performed the direct synthesis of aromatic polyamides employing triphenyl phosphite (TPP) as activator. Only low molecular weight *para*-oriented polyamides were obtained with their original method.

In 1982 Higashi et al. (2) found a great improvement of the inherent viscosity (η_{inh}) value of poly(*p*-phenylene terephthalamide) (PPD-T) by adding to the solvent medium a salt mixture composed of $CaCl_2$ and LiCl, instead of LiCl alone, as previously suggested by Yamazaki et al. (3). However, their attempts to also use the double salt system in the synthesis of poly(*p*-benzamide) (PBA) did not provide any η_{inh} improvement. Later on, Preston and co-workers (4, 5) found that the optimum temperature for the direct synthesis of both polymers is 115°C.

Recently we reported that, when very accurate purification

procedures are used, the inherent viscosities of PPD-T and PBA can reach rather high values (6). In the case of PPD-T, the η_{inh} value obtained in our laboratory is very close to that of the same polymer synthesized by using terephthaloyl chloride, which is used in all industrial recipes instead of the corresponding diacid.

In the present paper we report a systematic study of the role of several reaction parameters in order to evaluate the best experimental conditions for the direct synthesis of PPD-T and PBA, taken as examples for AA-BB and A-B polyamides, respectively.

In particular, we studied the effect of temperature, salt type and concentration, amount of TPP and its stepwise introduction, under both Yamazaki and Higashi conditions. With the above terms, we designate a reaction medium based on *N*-methyl pyrrolidone (NMP), pyridine (Py), and triphenyl phosphite (TPP), plus lithium chloride or lithium and calcium chlorides, respectively. Within each system, component (including monomer or reactants) concentrations can largely be varied. The slight discrepancy between the optimum η_{inh} values quoted in the present paper (see later) and those found previously (6) is due to minor differences in the purification procedures and polymerization setups.

Experimental section

(a) Materials

NMP (Aldrich) was refluxed under vacuum in the presence of CaH_2 for 8 h and distilled under the same conditions. Then it was refluxed under vacuum in the presence of P_2O_5 for 6 h and dis-

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tilled; the treatment was repeated twice. Py (Aldrich) was refluxed under an inert atmosphere in the presence of sodium hydroxide for 6 h and distilled; the treatment was repeated three times. LiCl (Carlo Erba) and CaCl₂ (Fluka) were dried for 24 h at 340°C under vacuum. TPP (Aldrich) was purified by fractional distillation under vacuum. The procedure was repeated three times. Diphenyl phosphite (DPP), Aldrich, was purified by fractional distillation under vacuum. The procedure was repeated three times. *p*-Phenylenediamine (PPD), Fluka, was purified by sublimation at reduced pressure. The procedure was repeated three times. Terephthalic acid (TA), Amoco, was dried for 24 h at 80°C under vacuum. *p*-Aminobenzoic acid (pABA), Aldrich, was dried for 24 h at 100°C under vacuum.

(b) Procedure

1. Synthesis of PBA in a solvent medium containing LiCl (so-called Yamazaki conditions)

In a typical run, by operating in a dry-box under inert atmosphere, 10 mL of NMP, 3.3 mL of Py, 1.37 g of pABA, 1.70 mL of TPP, and 0.5 g of LiCl were added to a 50 mL three-neck flask, fitted with an inlet and an outlet for inert gas (in most cases argon) and a magnetic stirrer. Oxygen traces were preliminarily removed from the components mentioned above by several cycles of vacuum and argon. The vessel was placed in a thermostatically controlled oil bath at 115°C. The reaction mixture became a clear gel within 0.5 h. After 4 h of reaction, the polymer obtained was ground in a blender in the presence of methanol. The reaction product was washed with boiling methanol and dried in a vacuum oven for 18 h at 80°C. Polymer yield was determined gravimetrically.

2. Synthesis of PBA in a solvent medium containing LiCl and CaCl₂ (so-called Higashi conditions)

NMP (25 mL), Py (5 mL), pABA (1.13 g), TPP (1.30 mL), CaCl₂ (1.5 g), and LiCl (0.5 g) were added to the above reaction vessel as described. All polymerization procedures and the operations on the resultant polymer were as mentioned in point 1.

3. Synthesis of PPD-T in a solvent medium containing LiCl (Yamazaki conditions)

In a typical run, 9 mL of NMP, 6 mL of Py, 0.3068 g of TA, 0.1997 g of PPD, 1.11 mL of TPP, and 0.4 g of LiCl were added to the above reaction vessel as described. All polymerization procedures and the operations on the resultant polymer were as mentioned in point 1.

4. Synthesis of PPD-T in a solvent medium containing LiCl and CaCl₂ (Higashi conditions)

In a typical run, 12.5 mL of NMP, 2.5 mL of Py, 0.2077 g of TA, 0.1352 g of PPD, 0.72 mL of TPP, 0.75 g of CaCl₂, and 0.25 g of LiCl were added to the above reaction vessel as described. All polymerization procedures and the operations on the resultant polymers were as mentioned in point 1 above.

(c) Polymer characterization

Viscosities, expressed as η_{inh} , of polymer solutions (at the concentration of 0.1 g/dL) were determined in 96% H₂SO₄ at 25°C using a Ubbelohde-type viscometer.

Results and discussion

In a recent paper (6) we reported on the critical relevance of high purification methods joined with very accurate polymer-

Table 1. Effect of [TPP]/[pABA] ratio in the synthesis of PBA (Yamazaki conditions).^a

| Sample | [TPP]/[pABA] | η_{inh} (dL/g) |
|--------|--------------|---------------------|
| 0.34 | 0.4 | 0.31 |
| 0.13 | 0.6 | 2.00 |
| 0.20 | 0.8 | 1.80 |
| 0.15 | 1.0 | 1.26 |

^aExperimental conditions: [pABA] = 0.75 mol/L; NMP/Py = 3 (v/v); 3.7% LiCl (w/v); T = 115°C.

Table 2. Effect of [TPP]/[pABA] ratio in the synthesis of PBA (Higashi conditions).^a

| Sample | [TPP]/[pABA] | η_{inh} (dL/g) |
|--------|--------------|---------------------|
| 0.21 | 0.4 | 0.10 |
| 0.18 | 0.6 | 1.53 |
| 0.19 | 0.8 | 1.38 |
| 0.12 | 1.0 | 1.40 |

^aExperimental conditions: [pABA] = 0.27 mol/L; NMP/Py = 5 (v/v); 1.7% LiCl (w/v); 5.0% CaCl₂ (w/v); T = 115°C.

ization procedures in order to obtain high molecular weight aromatic polyamides. In the present work, a systematic evaluation of various reaction parameters (see below) for both Higashi and Yamazaki conditions is explored, taking into account the aforementioned importance of high purification levels for all reaction components.

Namely, we studied the influence of variables such as TPP/monomer (or reactant) molar ratio, salt type and concentration, reaction temperature, and mode of TPP addition to the reacting mixture, in terms of both polymer yields (which were almost always quantitative) and polymer molecular weights (MW). The latter are hereafter reported in terms of inherent viscosities, i.e., true experimental values, instead of MW data calculated from still controversial $[\eta]$ -M relationships (7, 8).

The aromatic polyamides considered are PBA and PPD-T.

(a) Effect of the [TPP]/[monomer] or [TPP]/[reactant] ratio

1. [TPP]/[pABA]

We studied the synthesis of PBA prepared under Yamazaki or Higashi conditions and found that the best molar ratio for the synthesis of high molecular weight PBA was, in every case, [TPP]/[pABA] = 0.6. Thus, in Tables 1 (Yamazaki conditions) and 2 (Higashi conditions) are listed the η_{inh} values of PBA synthesized using different ratios of [TPP]/[pABA] (from 0.4 to 1.0). As shown in the tables, the inherent viscosity values decrease rapidly when [TPP]/[pABA] < 0.6, whereas such values for the two systems seems less prone to change at higher ratios.

2. [TPP]/[TA]

Table 3 lists the inherent viscosities of PPD-T synthesized under Yamazaki conditions, varying the molar ratio from 1.3 to 2.3 (a ratio of 2 refers to stoichiometric conditions). As we

Table 3. Effect of [TPP]/[TA] ratio in the synthesis of PPD-T (Yamazaki conditions).^a

| Sample | [TPP]/[TA] | η_{inh} (dL/g) |
|--------|------------|------------------------|
| 0.32 | 1.3 | 0.24 |
| 0.28 | 1.7 | 0.36 |
| 0.27 | 2.0 | 0.31 |
| 0.29 | 2.3 | 0.38 |

^aExperimental conditions: [TA] = [PPD] = 0.125 mol/L; NMP/Py = 1.5 (v/v); 2.7% LiCl (w/v); $T = 115^\circ\text{C}$.

Table 4. Effect of [TPP]/[TA] ratio in the synthesis of PPD-T (Higashi conditions).^a

| Sample | [TPP]/[TA] | η_{inh} (dL/g) |
|--------|------------|------------------------|
| 0.44 | 2.0 | 6.84 |
| 0.42 | 2.2 | 8.15 |
| 0.43 | 2.4 | 6.89 |

^aExperimental conditions: [TA] = [PPD] = 0.083 mol/L; NMP/Py = 5 (v/v); 1.7% LiCl (w/v); 5.0% CaCl₂ (w/v); $T = 115^\circ\text{C}$.

can see, the [TPP]/[reactant] ratio in this system seems to be less critical than in the PBA synthesis. Moreover, the inherent viscosity values of the resultant polymers are very low. This is probably due to polymer precipitation during the reaction, which thereafter proceeds in a heterogeneous phase.

The situation is sharply different for polymerization under Higashi conditions, with a total reagent concentration of 0.166 mol/L (Table 4) being used. In these experiments, no precipitation of the polymer is observed and a complete gelation of the reacting mixture appears to take place. Under these conditions, the growth of the polymer chains is surely more extensive than in the previous system.

(b) Effect of salt type and concentration

1. PBA

The types of salt dissolved in the reaction medium and the concentration of salts have been studied in detail. LiCl and CaCl₂ have been used alone or mixed together. Table 5, which is based on a [TPP]/[pABA] ratio = 0.6, gives the η_{inh} data obtained using different concentrations of salts.

The values obtained under experimental conditions indicated under footnote *a* are related to a monomer concentration of 0.75 mol/L. The maximum value obtained ($\eta_{inh} = 2.15$ dL/g) is higher than the best literature value (5) ($\eta_{inh} = 1.8$ dL/g), most probably because of a better purification of reagents and solvents. As can be seen from the table, the highest η_{inh} value for this relatively high monomer concentration corresponds to the synthesis where the largest total salt concentration has been used.

The values obtained under experimental conditions indicated under footnote *b* are related to a lower monomer concentration of 0.27 mol/L. It can be seen that the sample 0.18 has the lowest inherent viscosity. It may therefore be concluded that, in this system, CaCl₂ has a negative effect. The highest η_{inh} value (2.19 dL/g) has been obtained when a high salt con-

centration in the reaction medium, based on LiCl only, has been used.

It is known (3) that the main effect of salts dissolved in the solvent mixture is to increase the solubility of rigid polymer chains, allowing the synthesis to be carried out in a homogeneous phase. We may infer that a high salt concentration has a marked positive effect for systems leading to a high polymer concentration. On the other hand, when the polymer concentration is relatively low, the solubility problems for polyamides are less important, with a scant effect linked to the increase of salt concentration, in particular if CaCl₂ is present in the reaction mixture.

2. PPD-T

The nature of the salt is the most important parameter in the synthesis of this polymer. Our study has been focused on a [TPP]/[TA] ratio = 2.

The data obtained from experiments carried out under conditions indicated by footnote *a* in Table 6 are related to some syntheses carried out using a total reagent concentration of 0.25 mol/L. It is clear that the mixed salt system is the worst. In general, the η_{inh} values are very low and there are no big differences among the three values. This result is probably due to polymer precipitation during the synthesis, which makes further polymer growth unfavorable. In the same table, the data obtained from experiments carried out under conditions indicated by footnote *b* are related to syntheses performed at a total reagent concentration equal to 0.166 mol/L. By comparing these latter values with the previous ones, the importance of working with a lower reactant concentration in order to avoid polymer precipitation during the synthesis is clearly evident.

(c) Temperature effect

1. PBA

All above syntheses were made at 115°C , i.e., at the best conditions suggested in the literature (5). We considered it relevant to also check this assumption for the experimental conditions leading to the optimum data of our experiments. Table 7 gives the inherent viscosities of PBA synthesized under the best conditions previously quoted (Table 6), using reaction temperatures in the range of 105 to 120°C . Our data confirm the presence of a maximum value for the reaction at 115°C with $\eta_{inh} = 2.19$, as compared to 1.8 dL/g, quoted in the literature (5).

2. PPD-T

Table 8 refers to temperature effects on some syntheses made under Yamazaki conditions at [TPP]/[TA] ratio = 2.0. It is evident that this system is not very sensitive to the variation of temperature. The inherent viscosity values are rather low and almost constant.

More significant in this respect is the Higashi system. The data reported in Table 9 refer to syntheses made at a [TPP]/[TA] ratio of 2.2, which represents the best ratio found for these experimental conditions. The highest value is obtained at 115°C and is equal to 8.15 dL/g, much higher than the best literature value of 6.2 dL/g (5).

It is relevant to observe that the Higashi system is more sensitive to temperature variations than the Yamazaki system. It can also be seen that a dramatic decrease of η_{inh} occurs when

Table 5. Effect of salt type and concentration in the synthesis of PBA.

| Sample | LiCl (%; w/v) | CaCl ₂ (%; w/v) | LiCl + CaCl ₂ (%; w/v) | η_{inh} (dL/g) |
|-------------------|------------------|-------------------------------|--------------------------------------|------------------------|
| 0.13 ^a | 3.7 | 0.0 | 3.7 | 2.00 |
| 0.22 ^a | 3.7 | 11.3 | 15.0 | 2.15 |
| 0.24 ^a | 0.9 | 2.8 | 3.7 | 0.85 |
| 0.18 ^b | 1.6 | 4.8 | 6.4 | 1.53 |
| 0.28 ^b | 1.4 | 0.0 | 1.4 | 1.82 |
| 0.29 ^b | 6.7 | 0.0 | 6.7 | 2.19 |

^aExperimental conditions: [pABA] = 0.75 mol/L; NMP/Py = 3 (v/v); [TPP]/[pABA] = 0.6; T = 115°C.

^bExperimental conditions: [pABA] = 0.27 mol/L; NMP/Py = 5 (v/v); [TPP]/[pABA] = 0.6; T = 115°C.

Table 6. Effect of salt type and concentration in the synthesis of PPD-T.

| Sample | LiCl (%; w/v) | CaCl ₂ (%; w/v) | LiCl + CaCl ₂ (%; w/v) | η_{inh} (dL/g) |
|-------------------|------------------|-------------------------------|--------------------------------------|------------------------|
| 0.33 ^a | 2.7 | 0.0 | 2.7 | 0.32 |
| 0.30 ^a | 0.7 | 2.0 | 2.7 | 0.21 |
| 0.52 ^a | 0.0 | 3.5 | 3.5 | 0.24 |
| 0.51 ^b | 5.5 | 0.0 | 5.5 | 1.22 |
| 0.31 ^b | 6.7 | 0.0 | 6.7 | 1.16 |
| 0.34 ^b | 0.0 | 6.7 | 6.7 | 1.26 |
| 0.44 ^b | 1.7 | 5.0 | 6.7 | 6.84 |

^aExperimental conditions: [TA] = [PPD] = 0.125 mol/L; NMP/Py = 1.5 (v/v); [TPP]/[TA] = 2.0; T = 115°C.

^bExperimental conditions: [TA] = [PPD] = 0.083 mol/L; NMP/Py = 5 (v/v); [TPP]/[TA] = 2.0; T = 115°C.

Table 7. Temperature effect in the synthesis of PBA (Yamazaki conditions).^a

| Sample | Temperature (°C) | η_{inh} (dL/g) |
|--------|---------------------|------------------------|
| 0.35 | 105 | 1.70 |
| 0.44 | 110 | 1.66 |
| 0.29 | 115 | 2.19 |
| 0.43 | 120 | 1.53 |

^aExperimental conditions: [pABA] = 0.27 mol/L; NMP/Py = 5 (v/v); [TPP]/[pABA] = 0.6; 6.7% LiCl (w/v).

Table 8. Temperature effect in the synthesis of PPD-T (Yamazaki conditions).^a

| Sample | Temperature (°C) | η_{inh} (dL/g) |
|--------|---------------------|------------------------|
| 0.53 | 100 | 0.28 |
| 0.38 | 110 | 0.36 |
| 0.27 | 115 | 0.31 |
| 0.37 | 120 | 0.37 |

^aExperimental conditions: [TA] = [PPD] = 0.125 mol/L; NMP/Py = 1.5 (v/v); [TPP]/[TA] = 2.0; 2.7% LiCl (w/v).

Table 9. Temperature effect in the synthesis of PPD-T (Higashi conditions).^a

| Sample | Temperature (°C) | η_{inh} (dL/g) |
|--------|---------------------|------------------------|
| 0.49 | 107 | 7.71 |
| 0.42 | 115 | 8.15 |
| 0.48 | 122 | 6.27 |

^aExperimental conditions: [TA] = [PPD] = 0.083 mol/L; NMP/Py = 5 (v/v); [TPP]/[TA] = 2.2; 1.7% LiCl (w/v); 5.0% CaCl₂ (w/v).

the temperature is increased above the optimum value of 115°C.

(d) Mode of TPP addition

I. PBA

In 1984 Preston and co-workers (5) noticed that a direct synthesis of PBA from the dimer of the pABA, instead of the monomer itself, made it possible to obtain a polymer with a higher inherent viscosity. By this method, PBA with $\eta_{inh} = 4.6$ dL/g, as compared to the value of 1.8 dL/g for the polymer synthesized directly from pABA, was obtained and represents the highest value reached so far by the direct synthesis activated with TPP. In our opinion, an alternative and simpler route could produce

Table 10. Effect of TPP stepwise addition in the synthesis of PBA (Yamazaki conditions).^a

| Sample | [TPP]/[pABA] | η_{inh} (dL/g) | Increment (%) |
|-------------------|--------------|------------------------|------------------|
| 0.13 | 0.6 | 2.00 | — |
| 0.16 ^b | 0.6 | 2.25 | 13 |
| 0.15 | 1.0 | 1.26 | — |
| 0.17 ^b | 1.0 | 2.07 | 64 |

^aExperimental conditions: [pABA] = 0.75 mol/L; NMP/Py = 3 (v/v); 3.7% LiCl (w/v); $T = 115^\circ\text{C}$.

^bThe same as above; stepwise addition of TPP.

Table 11. Effect of TPP stepwise addition in the synthesis of PBA (Higashi conditions).^a

| Sample | [TPP]/[pABA] | η_{inh} (dL/g) | Increment (%) |
|-------------------|--------------|------------------------|------------------|
| 0.18 | 0.6 | 1.53 | — |
| 0.37 ^b | 0.6 | 1.96 | 28 |
| 0.12 | 1.0 | 1.40 | — |
| 0.36 ^b | 1.0 | 1.77 | 26 |

^aExperimental conditions: [pABA] = 0.27 mol/L; NMP/Py = 5 (v/v); 1.7% LiCl (w/v); 5.0% CaCl₂ (w/v); $T = 115^\circ\text{C}$.

^bThe same as above; stepwise addition of TPP.

relatively larger (as compared to the usual procedures) amounts of dimer in situ, by using a stepwise addition of TPP, thus initially activating only part of the carboxylic groups.

In Table 10, data concerning four syntheses made under Yamazaki conditions at a pABA concentration of 0.75 mol/L and two different [TPP]/[pABA] ratios are reported. Relevant improvements of η_{inh} , when TPP is added stepwise, were obtained.

The same conclusion can be reached from the data of Table 11, which refers to four syntheses performed using the more dilute pABA concentration of 0.27 mol/L under Higashi conditions. Also for this system a good improvement of inherent viscosity was found.

On this basis, a comparison between our highest η_{inh} value (sample 0.29 in Table 7), reached using a monomer concentration of 0.27 mol/L and 6.7% LiCl, and the corresponding η_{inh} value obtained from a synthesis made under the same conditions but with stepwise TPP addition, shows that under the latter conditions a further increase of η_{inh} (from 2.19 to 2.35 dL/g) was found. The above value is, probably, the highest η_{inh} obtained so far, when a direct synthesis from pABA is employed.

2. PPD-T

In contrast to PBA, the literature does not report, for the PPD-T synthesis, any improvement for the reaction made starting from the "dimer" (9). Similarly, in our stepwise procedure, no increase of η_{inh} was found.

(e) Use of DPP

As previously indicated, the best [TPP]/[pABA] ratio is 0.6, a rather unusual value if we consider that each TPP molecule

activates a carboxylic function, allowing it to react with the amino group. It can be reasonably assumed that DPP, formed as by-product during the reaction, is also able to activate the acidic group. Two attempts of PBA synthesis using DPP instead of TPP, for two different [phosphite]/[pABA] ratios were successful, although they gave rather low η_{inh} values, and fully justify our assumption. Thus, DPP can be considered to promote the reaction between the acid and the amino functions, although with lower efficiency. This may also be due to the presence of high concentrations of phenol not easily removed in our DPP. Phenol may be responsible, in our opinion, for the rather low η_{inh} values obtained (≤ 0.2 dL/g). Direct evidence of its role was demonstrated by its addition in equimolar amount to the monomer in a typical synthesis of PBA by TPP. The η_{inh} of PBA was lowered from 2.0 to 0.06 dL/g. Literature data on polyamidohydrazides synthesized in the presence of DPP, on the contrary, reveal that the latter is a better reagent than TPP (10).

Conclusions

Direct synthesis appears a very easy and useful method for obtaining, on a laboratory scale, aromatic polyamides characterized by a large range of inherent viscosity values, which depend on the experimental conditions, thoroughly studied in the present work, chosen for their synthesis.

In addition, accurate purification procedures and proper choice of the reaction conditions make it possible to reach quite high polymer molecular weights, close to those obtained by acyl chloride routes.

Advantages of direct synthesis are the ease to carrying it out, the use of relatively stable diacids instead of moisture-

and temperature-sensitive compounds, such as acyl chlorides, and also the simplicity and low cost of the experimental equipment.

On the contrary, the high concentration of TPP required, as well as the problems connected with its removal from the polyamide, may represent a relevant disadvantage.

Further improvement of the reaction can be envisioned by continually removing the phenol formed as by-product. As a consequence, it would be possible to shift the equilibrium more and more towards the products and avoid the possibility of the phenol reacting with the growing polymer chains.

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