High Molecular Weight Aromatic Polyamides by Direct Polycondensation

Saverio Russo* and Alberto Mariani

Dipartimento di Chimica dell'Università, via Vienna 2, 07100 Sassari, Italy

Vladimir N. Ignatov and Igor I. Ponomarev

Academy of Sciences of Russia, A.N. Nesmeyanov Institute of Organo-Element Compounds, Vavilov Street 28, 117334 Moscow, Russia

Received March 30, 1993
Revised Manuscript Received July 6, 1993

Introduction. The synthesis of aromatic polyamides is generally performed by using activated derivatives of aromatic acids such as acyl chlorides.[1-4] In 1974 Yamazaki and Higashi[5] developed a new method of direct synthesis employing triphenyl phosphite (TPP) as an activator. However, only low molecular weight polyamides were obtained with their original method. In 1982 Higashi *et al.*[6] found an improvement in the inherent viscosity (η_{inh}) of poly(*p*-phenylene terephthalamide) (PPDT) if $CaCl_2$ is added, in addition to LiCl, to the solvent mixture. However, the double salt system applied to poly(*p*-benzamide) (PBA) synthesis did not provide any improvement. Later, Krigbaum and Preston *et al.*[7,8] found that the best temperature is $T = 115$ °C for the synthesis of both polymers (namely, η_{inh} of PPDT = 6.2 dL/g at 25 °C and 0.1 g/dL).

We tried to duplicate Preston's results in the synthesis of PPDT, as part of our studies on matrix effects in direct polyamidation, which will be fully reported in a subsequent paper.[9] Initially, we only obtained PPDT samples characterized by $\eta_{inh} < 2$ dL/g, most likely because we adopted experimental procedures, commonly described in literature for purification of reagents and solvents, which were highly unsatisfactory in this respect.

In this work we describe the necessary procedures that allowed us to obtain PBA characterized by η_{inh} equal to 2.25 dL/g and PPDT of η_{inh} as high as 9.0 dL/g. For PBA, when obtained by direct polycondensation of *p*-aminobenzoic acid in the presence of TPP, to our knowledge the highest literature value is equal to 1.8 dL/g.[8]

For PPDT the value of $\eta_{inh} = 9.0$ dL/g is, probably, the highest value obtained so far, starting from terephthalic acid and *p*-phenylenediamine.

Experimental Section. (a) Materials. ***N*-Methylpyrrolidone** (NMP; Aldrich) was refluxed under vacuum in the presence of CaH_2 for 8 h and distilled in the same conditions. Then it was refluxed under vacuum in the presence of P_2O_5 for 6 h and distilled; the treatment with P_2O_5 was repeated twice.

Pyridine (Py; Aldrich) was refluxed in an inert atmosphere in the presence of NaOH for 6 h and distilled; the treatment was repeated three times.

LiCl (Carlo Erba) **and $CaCl_2$** (Fluka) were dried for 24 h at 340 °C under vacuum.

Triphenyl phosphite (TPP; 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 (T = 138 °C). 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.

Table I. Viscosity Data of PPDT Samples Synthesized from TA and PPD in the Presence of TPP

	Higashi[6]	Preston[7]	this work
η_{inh}	4.5[a]	6.2[b]	9.0[c]
$[\eta]$			9.4

[a] At 30 °C and c = 0.5 g/dL in concentrated H_2SO_4 (unknown concentration). [b] At 25 °C and c = 0.1 g/dL in concentrated H_2SO_4 (unknown concentration). [c] At 25 °C and c = 0.1 g/dL in 96% H_2SO_4.

(b) Polymerization of PPDT in a Solvent Medium Containing LiCl and $CaCl_2$. In a typical run, a 50-mL three-neck flask was fitted with an inlet and outlet for inert gas (in most cases, argon) and a magnetic stirrer. Amounts of 25 mL of NMP, 5 mL of Py, 0.4154 g (0.0025 mol) of TA, 0.2704 g (0.0025 mol) of PPD, 1.70 g (0.0055 mol) of TPP, 1.5 g of $CaCl_2$, and 0.5 g of LiCl were added to the reaction vessel. Oxygen traces in the above solvents were preliminarily removed by several cycles of vacuum and argon. All operations were carried out in a drybox under an inert atmosphere in order to avoid humidity and air. The vessel was placed in a thermostatically controlled oil bath at T = 115 °C. The reaction mixture became a clear gel in 18–28 min. After 4 h of reaction the gel was ground in a blender in the presence of methanol. The polymer was washed with boiling methanol and dried in a vacuum oven for 18 h at 80 °C.

(c) Polymerization of PBA in a Solvent Medium Containing LiCl and $CaCl_2$. (1) Whole Initial Addition of TPP. In a typical run, 25 mL of NMP, 5 mL of Py, 1.13 g (0.0082 mol) of pABA, 1.56 g (0.0050 mol) of TPP, 1.5 g of $CaCl_2$, and 0.5 g of LiCl were added to the above reaction vessel following the described procedure. All operations on the resultant polymer were as above.

(2) Stepwise Addition of TPP. By operating as described in point (1), 0.78 g (0.0025 mol) of TPP were added to the reaction vessel from the beginning and another 0.78 g was stepwise added in 30 min.

(d) Polymerization of PBA in a Solvent Medium Containing LiCl. (1) Whole Initial Addition of TPP. In a typical run, 10 mL of NMP, 3.3 mL of Py, 1.37 g (0.01 mol) of pABA, 2.01 g (0.0065 mol) of TPP, and 0.5 g of LiCl were added to the reaction vessel described above. The reaction mixture became a clear gel in 27 min. All operations on the resultant polymer were as described in point (b).

(2) Stepwise Addition of TPP. By operating as described in point (1), 1.12 g (0.0036 mol) of TPP were added to the reaction vessel from the beginning and another 0.89 g was stepwise added in 22 min. The reaction mixture became a clear gel in 35 min.

(e) Viscosity Measurements. The viscosity measurements were made in 96% H_2SO_4 (Carlo Erba) solutions at 25 °C by using an Ubbelohde viscometer.

Results and Discussion. The inherent viscosity of a PPDT sample of ours compared with literature values from Higashi *et al.*[6] and Preston *et al.*[7] is reported in Table I. Most probably, Preston's data[7] represent the highest literature values obtained so far, among those referred to PPDT synthesized directly from terephthalic acid and *p*-phenylenediamine. It can be seen that, by using our purification and reaction procedures, it is possible to obtain PPDT with a much higher inherent viscosity, comparable to, if not better than, that of many industrial PPDTs obtained from terephthaloyl chloride and PPD.

A comparison between our data on PBA η_{inh} and the best literature values[8] is given in Table II. The use of

0024-9297/93/2226-4984$04.00/0

Table II. Inherent Viscosity of PBA Samples Synthesized from pABA in the Presence of TPP (Added at the Beginning of the Reaction)

	Preston[8]	this work
with LiCl	1.8[a]	1.94[b]
with LiCl/$CaCl_2$		1.72[b]

[a] At 25 °C and c = 0.1 g/dL in concentrated H_2SO_4 (unknown concentration). [b] At 25 °C and c = 0.1 g/dL in 96% H_2SO_4.

Table III. Influence of the TPP Mode of Addition on PBA Inherent Viscosity

	whole initial addition	stepwise addition
with LiCl	1.94[a]	2.25[a]
with LiCl/$CaCl_2$	1.72[a]	2.05[a]

[a] At 25 °C and c = 0.1 g/dL in 96% H_2SO_4.

LiCl instead of a LiCl/$CaCl_2$ mixture in the solvent medium is confirmed to be preferable for PBA synthesis.

An attempt to minimize TPP thermal decomposition and formation of phenol has been pursued by gradually introducing it during the reaction. Inherent viscosity values referred to PBA samples prepared by stepwise introduction of TPP (before the gel onset) are given in Table III. It can be noticed that these values are, in both cases, higher than those obtained for samples prepared by an initial introduction of the whole TPP in the reaction mixture (see Table II). On the contrary, no significant differences in the inherent viscosity of PPDT samples have been found when the same stepwise introduction of TPP has been applied to this system and compared to the usual procedure. At present, no easy explanation for this opposite behavior in the synthesis of PBA and PPDT has been found.

From our preliminary results it can be suggested that accurate purification of all ingredients, together with optimization of the experimental procedure, can allow us to obtain a product characterized by molecular weights similar to, if not higher than, those of PPDT products formed from the diacyl chloride. Further studies are in progress.[9]

Acknowledgment. Support from 40% MURST funds is gratefully acknowledged. V.N.I. is indebted to the International School of Advanced Polymeric Materials (Ferrara) for providing a fellowship.

References and Notes

(1) Morgan, P. W. *Macromolecules* **1977**, *10*, 1381.
(2) Kwolek, S. L.; Morgan, P. W. *Macromolecules* **1977**, *10*, 1390.
(3) Morgan, P. W. *Condensation Polymers by Interfacial and Solution Methods*; Interscience: New York, 1978; pp 141–165.
(4) Vollbracht, L. *Comprehensive Polymer Science*; Pergamon Press: Oxford, U.K., 1989; Vol. 5, pp 375–386.
(5) Yamazaki, N.; Higashi, F.; Kawabata, J. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 2149.
(6) Higashi, F.; Ogata, S.-I.; Aoki, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 2081.
(7) Krigbaum, W. R.; Kotek, R.; Mihara, Y.; Preston, J. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 4045.
(8) Krigbaum, W. R.; Kotek, R.; Mihara, Y.; Preston, J. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 1907.
(9) Russo, S.; Mariani, A.; Ignatov, V. N., to be published.